INEEL/EXT-02-00233
Revision 1
Project No. 23378

Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites

Volume 1, Technology Description and Treatability Study Results for Operable Unit 7-13/14

Guy G. Loomis
James J. Jessmore
Jerry R. Weidner
Christopher M. Miller
Allen L. Sehn
June 2003

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

INEEL/EXT-02-00233
Revision 1

Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites

Volume 1, Technology Description and Treatability Study Results for Operable Unit 7-13/14

Guy G. Loomis
James J. Jessmore
Jerry R. Weidner
Christopher M. Miller[a]
Allen L. Sehn[a]

June 2003

Idaho National Engineering and Environmental Laboratory
Idaho Completion Project
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727

---

a. University of Akron in Akron, Ohio.

ABSTRACT

This report discusses in situ grouting in two volumes. Volume 1 summarizes the technology and presents results of a treatability study conducted by the Idaho National Engineering and Environmental Laboratory. Volume 2 estimates the durability and chemical buffering properties of grouted waste monoliths in the subsurface of the Radioactive Waste Management Complex at the Idaho National Engineering and Environmental Laboratory. In addition, Volume 2 provides the results of numerical simulations pertaining to contaminant mass release, monolith freeze/thaw durability, and monolith seismic stresses.
In situ grouting involves the injection of grout at high pressure (jet grouting) into a buried waste site. The grouting action creates a solid monolith with reduced permeability and increased subsidence control. Testing described in Volume 1 involves three phases: bench testing, implementability testing, and full-scale field testing. The treatability study is being performed to determine the efficacy of using in situ grouting as a buried waste treatment at the Idaho National Engineering and Environmental Laboratory's Waste Area Group 7, Operable Unit 13/14, located in the Subsurface Disposal Area of the laboratory's Radioactive Waste Management Complex. Data presented in this report will be used in the Waste Area Group 7-13/14 Comprehensive Remedial Investigation/Feasibility Study, which is part of the Comprehensive Environmental Response, Compensation, and Liability Act process for Superfund sites such as the Subsurface Disposal Area.

EXECUTIVE SUMMARY

This report discusses in situ grouting in two volumes. Volume 1 summarizes the technology and presents the results of testing conducted for an in situ grouting treatability study performed by the Idaho National Engineering and Environmental Laboratory (INEEL). Volume 2 contains the results of analytical calculations estimating the long-term durability of the monoliths created by the grouting technology and on the long-term performance of a treated buried waste site relative to containment release. Volume 2 uses analytical techniques and the support data discussed in Volume 1. In situ grouting involves applying grout at high pressure (jet-grouting) to a buried waste site, creating solid monoliths with reduced permeability and increased subsidence control. Testing described in this volume involves three phases: bench testing, implementability testing, and full-scale field testing. The treatability study is being performed to determine the efficacy of using in situ grouting as a buried waste treatment at the Waste Area Group 7 (WAG-7), Operable Unit 13/14, located in the Subsurface Disposal Area (SDA) of the INEEL's Radioactive Waste Management Complex (RWMC). Data presented herein will be used in the WAG 7-13/14 Comprehensive Remedial Investigation/Feasibility Study, which is part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process for Superfund sites such as SDA.

In situ grouting creates solid monoliths from unconsolidated buried waste sites using jet grouting of specialty grouts. The technology was developed for remediation of the transuranic pits and trenches at the INEEL. However, the technology has also been applied to stabilize contaminated soil sites, specifically the Acid Pit at the SDA. The process involves high-pressure (nominally 400 bar [6,000 psi]) injection of specialty grouts directly into the waste via a drill string with injection nozzles at the bottom. The drill string is driven into the waste on a nominally 50-cm (20-in.) triangular pitch, and the rotating drill string is withdrawn in precise increments creating a column of grouted waste. By interconnecting the columns, a solid monolith is formed that eliminates the potential for subsidence, reduces the local hydraulic conductivity, and, by using specialty grouts, can retard or eliminate the release of contaminants to the ground water. The unique feature of the in situ grouting technology is the inclusion of a contamination control system involving a thrust block and drill string shroud that contains any transuranic contaminants mobilized during grouting.

Specific results of the in situ grouting treatability study are given below and include those from bench, implementability, and field studies. Bench studies involved a complicated testing protocol designed to first choose three grouts from six candidates for use in implementability testing that involved full-scale field grouting equipment. Bench data are also obtained to support monolith durability estimates and transport modeling efforts discussed in Volume 2. Implementability testing compared three grouts, and one was chosen for use in field testing. Finally, a limited field demonstration of the technology was performed in which contamination control data are discussed in detail.

Six candidate grouts for bench testing included TECT HG™ (cementitious), U.S. Grout (cementitious-pozzlonic), GMENT™-12

(cementitious-pozzlonic), Enviro-Blend® (phosphate based), Waxfix™ (molten paraffin based), and Saltstone (mostly pozzlonic). All of these grouts displayed the potential to be jet-groutable. In fact, TECT HG and Waxfix had been applied before at the INEEL. The bench tests first screened the grouts for basic grouting parameters including gel time, temperature of set, viscosity, and density. The only grout eliminated due to an early gel time (less than 2 hours) on this initial screening was Saltstone. A gel time of 2 hours was chosen to avoid "flash setting" of the grout in pumping equipment.

It was concluded that with some reformulation effort (beyond the scope of this study) that the Saltstone could be considered for application. Waxfix had special screening criteria because criticality concerns required that a neutron absorber be uniformly distributed in the grout during a multiday cooldown period. Specifically, there was a requirement that boron-10 be suspended in a cooling column of Waxfix at a concentration of 1 g/L. Using a glycerin solution of sodium tetraborate as the source of boron-10, there was almost a complete settling of the boron during cooldown, which eliminated Waxfix from further consideration in this study. However, subsequent analytical studies show that a uniform suspension is possible. Including Waxfix as a candidate grout is desirable in that past studies demonstrated that extensive penetration of grout into the soil/waste matrix is achievable. Additionally, Waxfix could be applied as an aid to retrieving buried transuranic waste as a contamination control measure during waste excavation and subsequent processing. This initial screening left TECT HG, U.S. Grout, Enviro-Blend, and GMENT-12 for further testing.

These four remaining grouts were tested as a neat grout for compressive strength, hydraulic conductivity, leaching using American Nuclear Society (ANS) 16.1, measurement of oxidation-reduction potential (eH) and acid-base properties (pH) during the ANS 16.1 leaching procedure, tensile strength, and effect on compressive strength due to the presence of interferences (commonly seen interferences that might affect grout curing in the transuranic pits and trenches include organic sludge, soil, and nitrate salts). Based on the interference tolerance testing, a selected weight-percent mixture of neat grout and the interferences (either 50 wt% soil, 9 wt% organic, or 12 wt% nitrate salts) was formulated and tested for ANS 16.1 leaching with pH and eH measured for each leachate, compressive and tensile strength, and hydraulic conductivity. Other special testing designed for the in situ grouting application included a microencapsulation test in which neat grout is mixed with an organic sludge containing trichloroethane (TCA), trichloroethylene (TCE), carbon tetrachloride (CCl_4), and tetrachloroethylene (PCE). Once mixed, the cured sample is inserted into a special control volume chamber in which the air space is sampled every 10 days for a total of 90 days to establish a rough order of magnitude of the rate of diffusion for the various volatile organic compounds (VOCs). In addition, a special macroencapsulation test was performed in which a cylindrical sample of cured grout with a cavity in the center was filled with organic sludge and sealed at the end to measure the diffusion of VOCs through the matrix. This macroencapsulation test was performed in the same special control column chamber used in the microencapsulation test.

Based on an evaluation of the results from the testing protocol discussed above, three of the grouts were further down-selected including TECT HG, U.S. Grout, and GMENT-12 (Enviro-Blend was eliminated). The three chosen grouts displayed excellent compressive and tensile strength characteristics, with neat grout values in the 161–466 bar (2,500–7,000 psi) range for compressive strength. Enviro-Blend displayed poor cured strength only in the "hundreds" of psi range. More importantly, the three grouts displayed good tolerance to interference materials such as organic sludge, soil, and nitrate salts relative to compressive strength. In general, compressive strengths above 1,000 psi were obtained with up to 9 wt% organic sludge, 50 wt% soil, and 12 wt% nitrate salts. On the other hand, Enviro-Blend had no tolerance to the interferences.

ANS 16.1 leach data (as leach index), showed that Enviro-Blend was superior to the three down-selected grouts due to the presence of phosphate in the grout (the three selected grouts displayed ANS 16.1 leach indexes in the range from 10 to 13, with Enviro-Blend measured at 15). During these leaching tests, the eH and pH were measured in the leachate water and found to be in the range of 9.6 to 11.4 for pH and less than 313 mV for eH, suggesting compatibility with the INEEL basic soil. Hydraulic conductivity was measured for the selected grouts in the e-9 cm/s range. For Enviro-Blend, the value was e-7 cm/s, which is two orders of magnitude lower than for the selected grouts. Interestingly, even with the presence of the interferences (nitrate at 12 wt%, soil at 50 wt%, and organic sludge at 9 wt%), hydraulic conductivity for the chosen grouts was not degraded much below the e-9 cm/s range. Based on an elaborate weighting criterion, all of the test results were applied to the four candidate grouts, resulting in a score of 4,184 for TECT HG, 4,150 for U.S. Grout, 3,862 for GMENT-12, and 3,010 for Enviro-Blend. Based on this ranking system, TECT HG, U.S. Grout, and GMENT-12 were recommended for implementability testing.

Other data obtained during the bench study were results from a specially designed micro and macro encapsulation study for VOC release from the grout. The micro test involved intimately mixing neat grout with organic sludge and measuring the gas release rate of the various VOCs integral to the sludge. In the macro test, a neat grout cylinder with a hollow core was created, and the organic sludge was placed inside the cylinder and sealed in place. For this case, the grout is assumed to be surrounding the sludge, which is a condition observed in previous field-scale demonstrations in simulated waste, and the movement of the VOCs is primarily one of diffusion. Results of this test were surprising in that it was found in the micro encapsulation test that there was only a release of VOC source term of the order of "hundredths" of a percent per 10-day testing period. This suggests that TECT HG, U.S. Grout, and GMENT-12 retard the flow of VOCs for possibly hundreds of years, which may be on the order of natural disintegration of the compounds in nature.

Volume 2 of this report takes the detailed data from the bench studies and formulates predictive models of contaminant transport and mechanisms of transport. Data important to these studies are the leach indexes, the physical properties, and the eH and pH of the leachate water in the ANS 16.1 testing.

Implementability full-scale field testing was performed to down-select the three grouts recommended from the bench study. These studies also gave performance data such as mixability, groutability (ease of jet grouting) and cleanup properties for those grouts that had never been grouted before. This testing involved creating triplex columns on a 50-cm (20-in.) triangular pitch in INEEL-like silty-clay soils. During this testing, it was demonstrated with full-scale field equipment that the three grouts recommended from the bench testing (TECT HG, U.S. Grout, and GMENT-12) could be applied for in situ grouting. All three grouts could be mixed and delivered at 400 bar (6,000 psi) via jet grouting. U.S. Grout and GMENT-12 required using a 2.4-mm nozzle to achieve the desired (ease of mixing) 400 bar (6,000 psi), and the third grout could pressurize the system using a 3-mm nozzle. The size of the nozzle is important in that the larger the nozzle the less prone to plugging from small debris in the system or the effects of filter-caking in a stagnant condition. Also demonstrated at the implementability testing was the ability to place a 7-cm (2.75-in.) polyethylene rod into a just-grouted hole for proof of concept that removal of the rod after grout cure would result in a complete borehole for performing hydraulic conductivity tests.

GMENT-12 was chosen from the three grouts based on factors such as basic cost, ease of mixing and cleanup of the grout, minimized grout returns in creating a triplex column, and formation of the monolith. All three grouts displayed the capability to be jet grouted and form solid stand-alone monoliths in an INEEL-type soil condition (tightly packed silty-clay soils). This soil condition is thought to be the most restrictive for jet grouting due to a lack of voids compared with the buried debris case, where the voids are much increased over a soil-only condition. U.S. Grout had noticeably higher grout returns due to a lower specific gravity than the other grouts (U.S. Grout 1.6, GMENT-12 1.84, TECT HG 2.16). After grouting two holes with U.S. Grout, the space under the simulated thrust block was filled with grout and the third hole could not be grouted. With a lower specific gravity grout, there is not as much kinetic energy imparted to the surrounding medium as with the higher specific gravity grouts, the velocity of the grout being the same. An evaluation of ease of mixing and cleanup properties for TECT HG and GMENT-12 showed GMENT-12 with a slight edge; therefore, GMENT-12 was selected as the single grout to be carried into field testing.

During the field test, a total of 12 holes were grouted using the thrust block/shroud concept. This concept involves a glovebox-like structure placed over the pit called a thrust block. Plastic sleeves are attached to the thrust block for each predetermined hole. Prior to grout injection, the plastic sleeves are attached to the drill string shroud, forming a seal. The drill string is inserted through a plastic diaphragm in the thrust block to allow drilling, then grouting. When finished, the drill string is withdrawn, and the plastic sleeve is "J" sealed using duct tape.

Even though an injury accident occurred after successfully grouting only 12 holes, considerable data on using the thrust block concept and actual data on the capability of the thrust block to contain the terbium tracer were obtained. It was planned to grout 114 holes and perform an elaborate excavation of the monolith; however, the project was not completed. The main reason was the need to redirect remaining budget for more pressing INEEL projects. At the time, the cost of restart would have been prohibitive, requiring new pressure relief systems and verification of operability, new procedures, and a vigorous operational readiness process.

As the test proceeded, operating procedures were perfected for using the thrust block concept. Since a trickle flow of grout through the nozzles had been utilized on all other grouting studies at the INEEL, this test represented the first attempt at grouting without allowing a continuous flow. During implementability testing, it was observed that following discontinuation of high-pressure flow, the drain of fluid in the drill stem was noted to be on the order of minutes. In fact, this knowledge was applied for the first two holes. For the first hole, the process worked as planned. When moving from the second hole to the third hole, the sack formed by the "J seal" twist and tape action on the thrust block sleeve filled with draining grout. Gravity pulled the sack full of fluid off the stinger, and the potentially terbium-contaminated neat grout flowed onto the top of the thrust block. This led to measurable terbium tracer on some of the thrust block smears.

This occurrence led to two corrective actions. One action was to separate the high-pressure hose at the fitting near the weather structure wall and relieve the vacuum in the drill stem (caused by the draining fluid that holds up material in the drill stem). In fact, compressed air was introduced to blow the grout out through the nozzles. The other action was to provide a separate bag at the bottom of the sack to help contain any dripping that may occur at the J seal. In an actual radioactive application, however, it would be desirable to have a special self-cleaning relief valve in the system to relieve the vacuum and the possible automatic actuation of compressed air to blow out the remaining grout.

Another major issue was the amount of nozzle plugging and time spent using rotopercussion to unstick plugged nozzles. This issue may be related to the grout chosen for the test (GMENT-12). In prior studies using TECT HG, there was an allowed trickle flow for most of the grouting; however, there were times when the grout was stopped and startup was accomplished without significant plugging of the nozzles.

Prior to discontinuation of testing, all systems were working as planned, with minor modifications required. These modifications include the need for a better view of the void space under the thrust block using remote TV cameras. Another minor modification to the thrust block design would be to provide a deeper Lexan well in that the TV cameras were not deep enough in the various camera wells to get a perfect wide-angle view of the spaces under the thrust blocks. Another minor modification would be to provide a hard pipe for the inlet and outlet of the thrust block high-efficiency particulate air filtration system to avoid collapse of the hose. It was obvious that a better weld connection of the shroud to the top bracket was required as well as an engineered twist in the shroud material itself to avoid the rotating drill steel from touching the inner shroud as the drill string was inserted and withdrawn from the test pit.

During the test, grout was mixed in Idaho Falls at a Ready Mix plant and transported 80 km (50 miles) to the INEEL Cold Test Pit South three times a day (3,024 L [800 gal] per trip). This distance led to poor utilization of mixed grout in that many loads were dumped unused, having begun to set before they could be injected. When the grout actually arrived at the Cold Test Pit, the grouting system had not been functioning for the entire 2 hours, and a full truck was still available. The obvious solution is to utilize a mobile ready-mix plant at the Cold Test Pit.

During the limited field demonstration, several lessons were learned. Some of the lessons were related to operations of the system and others were system related due to the experienced catastrophic failure of a high-pressure fitting.

During operations in the field, the most basic problem with the system was nozzle plugging related to the fact that no trickle flow of grout was allowed by the thrust block/shroud contamination control system. Because this system disallows a trickle flow of grout (in past studies trickle flow was the technique to keep the nozzles clear), a completely new design of a vacuum relief system within the drill string is needed. This vacuum relief system is needed to allow complete draining of the drill string of neat grout immediately after grouting and prior to moving the drill string to a new hole. Following grouting, simply letting the drill string drain its fluid was not sufficient in that the vacuum created by partially draining the drill string held up fluid that once jostled upon moving the system, causing fluid to drain into the plastic sleeve that had been taped off.

Lessons learned relative to the high-pressure system failure include the following: The grouting subcontractor should install a high-pressure relief valve and a redundant-pressure relief plug to allow emergency bleeding of the system. The primary system would be a valve, and the secondary system could be a simple plug located in an easily and safely accessed area. This emergency plug should allow safe, easy access for tools in the event of a system pressurized by nozzle plugging. Once the plug has been forced open in an emergency, it should be replaced with a new plug and/or fitting. In addition, as part of the emergency procedure, the relief system should be cleaned or replaced to allow proper operation. The grouting contractor should also reevaluate the position of personnel working on the high-pressure equipment and perhaps employ shielding from high-pressure fittings. The grouting subcontractor should check the setting on the automatic shutoff feedback switch prior to each use. This will require a pressurization procedure using water and may require special plumbing to accomplish the testing.

The incident at the Cold Test Pit suggests rapid uncontrolled overpressurization by the triplex pump not shown on the gauges. Specifically, if a nozzle plugs, the operator needs overpressurization protection independent of the gauges. The grouting contractor should use only pressure gauges that operate smoothly at all pressures. It is speculated that the gauge used during the field test sticks at lower pressures and unsticks at higher ones. For instance, the gauge can read 20 bar when it is really 500 bar, about to go to 1,000 bar with a few more strokes of the triplex pump. It is recommended that there be two gauges, one used during low-pressure operations and another used during high-pressure ones. It is suggested that the low-pressure gauge be valved in to operate at low pressures and valved out when operating at high pressures. The most obvious lesson learned is that the grouting contractor should use only rated equipment and fittings such as valves, hoses, and whip-checks. Whip-check and fitting documentation should accompany the fittings and indicate an operating pressure at the design pressure of the pump with an appropriate safety factor. A shield should be installed around the outlet to the high-pressure pump to deflect any future blowout due to catastrophic failure of any fittings in the vicinity of the high-pressure pump.

Data quality objectives were listed in the test plans covering the bench, implementability, and field testing phases of the treatability study. Most of the data quality objectives discussed in the test plans were addressed by the treatability study. However, there are definite, missing gaps in data due to truncation of the field-testing program. All of the data quality objectives were met for the bench and implementability testing phases. With limited testing in the field testing phase, many of the objectives associated with the field testing involving the thrust block and contamination control system were addressed. Overall, the main data quality objective relating to implementability of the in situ grouting process using the thrust block contamination control system was demonstrated. Only minor design changes are required as discussed above.

The overall grouting process is not as rapid on a time-per-hole basis compared with that expected using alternative grouting concepts (the x-y positional system discussed later in the report). However, the thrust block design could be applied for a variety of applications in buried waste regions. For instance, the thrust block concept could be used to grout a series of interconnected columns (say 10-hole columns) at various regions within a pit to support a cap and leave the thrust block in place. Another application would be to grout small very specific hot spots within a buried waste region. The time issue only becomes important when treating large areas on the order of hundreds of thousands of holes over a 10-year period. Finally, to fully evaluate the missing data quality objectives (those relating to the characteristics of the emplaced monolith like void filling, and monolith durability), would require completion of the grouting in the pit followed by hydraulic conductivity testing and excavation of the monolith with further chemical and physical testing of samples from the resultant monolith.

The following conclusions stem from the in situ grouting studies:

In situ grouting of buried transuranic waste using the thrust block concept is technically feasible at the INEEL with several modifications to the system. Modifications include developing a better pressure relief system to facilitate draining of fluid in the drill stem. Inclusion of an additional plastic shield over the J-seal layer would avoid minor dripping of grout when moving the system. By using double screening in the grout preparation phase, potential debris in the grout that could block nozzles can be avoided. Finally, modifications to the shroud assembly that would prevent wear on the inner shroud and disallow detachment at the upper bracket are required.

A variety of grouts are available for application to jet grouting. Grouts tested in this study that were shown to be jet groutable include TECT HG, U.S. Grout, and GMENT-12. With minor modifications, the paraffin-based Waxfix and Saltstone grout could most likely also be candidate grout materials. By reformulation of American Minerals, Inc.'s Enviro-Blend grout, it too could be considered a candidate grout.

Bench studies of U.S. Grout, TECT HG, Enviro-Blend, and GMENT-12 show excellent retention of constituent elements and tracer materials during ANS 16.1 leach testing. Bench studies suggest that U.S. Grout, TECT HG, and GMENT-12 show a strong tolerance to interferences commonly occurring within the buried waste including organic sludge (up to 9 wt% tolerance), soil (up to 50 wt% tolerance), and nitrate salts (up to 12 wt% tolerance). Bench studies of VOC retention show that there is only a few hundredths of a percent of source term lost per 10-day interval in special microencapsulation testing involving cured mixtures of neat grout and 9 wt% organic sludge (for U.S. Grout, TECT HG, and GMENT-12).

The contamination control features of the thrust block/drill string shroud concept worked as planned. There was no terbium tracer spread to the high-volume air monitors, even though neat grout with potential terbium contamination was spilled onto the top of the thrust block (when the sack containing grout drippings fell off the drill string stinger). Inductively coupled plasma-mass spectroscopy of smears taken on the top of the thrust block following cleanup of the spill showed terbium contamination. Even with extensive foot traffic and movement of the drill rig over the spill location, there was no spread to the high-volume filters. It is hypothesized that the grout locks the tracer material up in larger, less easily aerosolizable particles. It is speculated that if the bag had not dropped, there would only have been terbium tracer within the containment of the drill string shroud and under the negative pressure of the thrust block in the grout returns.

Examination of the limited monolith created by grouting 12 holes showed a solid monolith with the usual inclusions of compacted clay soil. Embedded in the monolith was a drum containing nitrate salts partially filled with grout. Parts of the drum were filled with neat grout (where the voids were), and voids in the nitrate salt material had cured grout.

The following recommendations grow out of results of the in situ grouting studies:

There should be a tradeoff study comparing the thrust block concept and the x-y positional system remote grouting idea. The x-y positional system has been proposed as an alternative grout delivery system, which involves the drill rig mobilized by a remotely controlled gantry crane. In principle, the x-y positional system answers all the problems encountered with the thrust block concept. With the x-y positional system, a trickle flow of grout can be allowed and there are no real limitations on grout returns, which improves the chances of complete pit void filling. In addition, the x-y positional system has more flexibility when encountering large hard objects that might refuse the drill bit.

CONTENTS

FIGURES

TABLES

ACRONYMS

ANS	American Nuclear Society
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BBWI	Bechtel BWXT Idaho, LLC
BWXT	BWX Technologies, Inc.
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DE	Department of Energy
DOE	Department of Energy
DOE-ID	Department of Energy Idaho Operations Office
EWR	early waste retrieval
EXT	external
FL	Florida
HEPA	high-efficiency particulate air (filter)
HLW	high-level waste
HVAC	heating, ventilation, and air conditioning
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectroscopy
IDR	initial drum retrieval
INEEL	Idaho National Engineering and Environmental Laboratory
INEL	Idaho National Engineering Laboratory
LI	Leach Index
LLC	Limited Liability Company
NA	not applicable
NRC	Nuclear Regulatory Commission

NUREG/CR	Nuclear Regulatory Commission/contractor report
NW	northwest
PAC	powdered-activated carbon
PCE	perchloroethylene
PCE	tetrachloroethylene
PNNL	Pacific Northwest National Laboratory
PPE	personal protective equipment
PVC	polyvinyl chloride
RADCON	radiological control
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RPD	relative percent difference
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
SE	southeast
SW	southwest
TBD	to be determined
TCA	trichloroethane
TCE	trichloroethylene
TCLP	toxicity characteristic leaching procedure
TV	television
WAG	Waste Area Group
WSRC	Westinghouse Savannah River Company

Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites

Volume 1, Technology Description and Treatability Study Results for Operable Unit 7-13/14

1. INTRODUCTION

This report discusses in situ grouting in two volumes. Volume 1 summarizes the technology and presents the results of testing conducted for an in situ grouting treatability study performed by the Idaho National Engineering and Environmental Laboratory (INEEL). Volume 2 gives the results of analytical calculations on the long-term durability of monoliths created by the grouting technology and on the long-term performance of a treated buried waste site. Volume 2 uses analytical techniques and data discussed in Volume 1.

In situ grouting is the injection of grout at high pressure (jet grouting) to a buried waste site, creating solid monoliths for reduced permeability and increased subsidence control. Testing described in this volume involves three phases: bench, implementability, and full-scale field testing. The overall treatability study is being performed to determine the efficacy of using in situ grouting as a buried waste treatment at the Waste Area Group 7 (WAG-7), Operable Unit 13/14, located at the Subsurface Disposal Area (SDA) of the INEEL's Radioactive Waste Management Complex (RWMC). Data presented in this report will be used in the WAG 7-13/14 Comprehensive Remedial Investigation/Feasibility Study, which is part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process for Superfund sites such as the SDA.

Volume 1 of this report includes a summary of past technology development efforts related to in situ grouting as well as findings from the bench testing phase outlined in the bench test plan (Grant et al. 2000) and the implementability and field findings presented in the field and implementability test plan (Loomis 2001). The primary objective of both the bench and implementability studies was to down-select a single grout from a list of products under consideration for the final field test. These tests also provide key data for use in modeling the long-term risk of the resulting monolith created by in situ grouting. In addition to the test results, an estimate is given of the cost of application for the technology for remediation of transuranic pits and trenches.

Bench studies were performed at the University of Akron in Akron, Ohio, and involved a series of screening, physical, and chemical tests on six promising grouts applicable to the jet-grouting process. The study produced important data such as hydraulic conductivity, leaching, and dissolution information on the grouts as well as the tolerance of the grouts to interferences common in SDA buried waste. These data are essential to modeling efforts to predict long-term durability and performance of a grouted buried waste site. In Volume 2 of this report, the data are used to assess these long-term predictions.

The implementability tests were performed at the Richland, Washington, jet-grouting contractor site (Applied Geotechnical Engineering and Construction). In the implementability tests, three grouts down-selected from the bench testing were jet grouted at full scale, and a single grout was recommended for the full-scale field test, which was performed at the INEEL's Cold Test Pit South. This report describes the in situ grouting, provides the bench and field data, and evaluates results. In addition to giving test results, the report considers expected cost of operation in a radioactive mixed waste environment.

2. IN SITU GROUTING AND PAST EXPERIENCE

A series of in situ technologies have been developed for stabilizing mixed waste buried in landfills and contaminated soil sites. The technologies involve nonreplacement jet grouting to create a solid monolith from buried waste such that subsidence abatement is achieved while significantly reducing contamination migration. The monolith is created by jet grouting in a relatively tight pattern directly into the soil/waste matrix. The process has also been applied to buried waste as a pretreatment for eventual waste retrieval. The grout agglomerates fine geological media containing contaminants such that the normally dusty retrieval operation is performed relatively dust free. Full-scale field demonstrations have been performed in numerous simulated mixed waste sites. In addition, the technology has been applied to a contaminated mixed waste site.

Historically, subsurface containment strategies involve creating a vertical barrier wall and in some cases a horizontal barrier under the waste to create a “bathtub” around the contaminated zone. The jet-grouting technology creates a simultaneous horizontal and vertical barrier by forming a solid monolith of the buried waste as a form of in situ remediation. Another option is to retrieve the waste and process it for final disposal separately. The technology of jet grouting to create a monolith supports both of these potential remedial options. For the in situ disposal option, the resultant monolith is immune from subsidence, which can compromise any capping actions. In addition, the monolith lowers the water permeability through the material, thus reducing contaminant transport. If specially formulated grouting agents are used, some contaminants can also be chemically stabilized such that they are not soluble in water and thus not prone to leaching and migration.

Grouting agents considered by the INEEL are those that produce a solid matrix and are chemically neutral in the applied environment, thus representative of natural geological analogs. In addition, for the long-term disposal option, the grouting material is designed to be chemically and thermodynamically stable in the present burial environment, which would include a cap to eliminate freeze-thaw effects. For the in situ disposal option, it is assumed that as long as environmental effects do not change the chemical and thermodynamic equilibrium, the monolith can be considered stable for geological times (thousands to millions of years). This concept is important for transuranic waste with materials that have radiological half-lives on the order of 24,000 years in that modeling for these timeframes appears difficult.

For the retrieval option, the monolith produced by jet grouting causes contaminants and fine soils to be agglomerated into larger less aerosolizable particles, which improves the chances of controlling the spread of contaminants during retrieval and handling, especially for the plutonium-239/americium-241 particles. The first studies (Loomis and Thompson 1995) involved only the grout/retrieval concept. Later studies focused on the monolith concept for the in situ disposal option. Later studies involved testing a variety of grouting materials and strategies (Loomis, Thompson, and Heiser 1995; Loomis, Zdinak, and Bishop 1997). Most recently, the technology was extended to the creation of monoliths in contaminated soil zones (Loomis et al. 1999). Basically, the early studies resulted in an understanding of the need for balance between grout physical characteristics, jet grouting parameters, and resultant monolith development. What follows is a detailed description of how the technology is applied, followed by results of various full-scale studies performed on simulated mixed waste sites called pits.

2.1 Technology Description

The grouting apparatus consists of a CASA GRANDE JET-5 class high-pressure positive displacement pump, low-pressure feed pump with hopper assembly, CASA GRANDE C-6 class track-mounted drilling/grouting rig, and associated high-pressure hoses. A 9-cm-diameter drill stem is driven into the soil waste matrix using rotopercussion. Most insertions into buried debris are accomplished within 1-2 minutes of drill time. While drilling, a low-volume flow of grout is injected at the bit end of the nozzle to reduce friction and allow easier insertion.

The technology involves driving a drill stem through the waste and injecting grout at 400 bar (6,000 psi) through the rotating drill stem while withdrawing the drill stem in precise increments. Repeated applications on a nominal 50-cm triangular pitch matrix form a series of interconnected columns that eventually turn the soil/waste seam into a solid monolith. Contamination spread at the surface during drilling and grouting is reduced by using a specially designed "thrust block" and shroud assembly. This equipment contains the grout returns due to the high-pressure grouting process shown in Figures 1-3.

Figure 1 shows the basic glovebox nature of the thrust block assembly. Each hole has a diaphragm seal and a double plastic bag plus a metal recessed lid. Additionally, the thrust block is kept at negative pressure by using a high-efficiency particulate air (HEPA) filter also shown in Figure 1. Figure 2 shows the shroud around the drill stem and a plastic glove port in the thrust block with an "o" ring seal on the drill string housing that eliminates the spread of contaminants from the rotating contaminated drill stem. Figure 3 shows that following grouting, the drill steel is withdrawn and the plastic sack is twisted, taped, and cut. Besides providing a volume to collect grout returns during grouting, the thrust block offers a clean area for worker protection and adds a degree of shielding in the case of radioactive waste. In addition, the preformed holes through the thrust block have a pipe wiper material to clean the drill stem of contaminated material during withdrawal. The thrust block concept is applicable for large surface areas or small "surgical" applications of jet grouting.

An alternative concept for applying jet-grouting technology for buried transuranic waste is to use the x-y positional system, in which the drill string is suspended above a bermed area on a bridge crane. Use of this system has more widespread application for either buried transuranic waste or buried low-level but high gamma activity waste. This concept is described in full in Appendix A.

During field studies, a variety of grout materials were injected, including both single and dual materials as well as molten waxes. What follows is a description of test results.

2.2 Grouting with Single-Component Material

A series of materials have been jet grouted while successfully minimizing return of material to the surface. The jet-grouting action mixes the grout with the waste and interstitial soils to create monoliths in the buried wastes (Loomis and Thompson 1995; Loomis, Thompson, and Heiser 1995; Loomis, Zdinak, and Bishop 1997), thus providing for final in situ disposal. The test pits were typically constructed of containerized simulated waste material.

For these studies, the transuranic pits and trenches at the INEEL were used as a model. For these pits, typical waste consists of paper, cloth, wood, metal debris, concrete, asphalt, and various sludges delivered to the INEEL from the Department of Energy's (DOE) Rocky Flats Plant. The wastes were originally containerized in metal drums and plywood boxes. Some of the waste has been buried in shallow pits for up to 40 years, such that the containers have been destroyed. For testing purposes in the simulated pits, cardboard boxes and drums are used to simulate long-term aging of the containers in an actual pit.

For the single-component materials, grout is forced through two nozzles located 180 degrees apart on the bottom of the drill stem. The nozzles are offset 5 cm to maximize waste coverage in creating a column. At the bottom of the drill stem is usually a conical drive point to facilitate driving the rotating

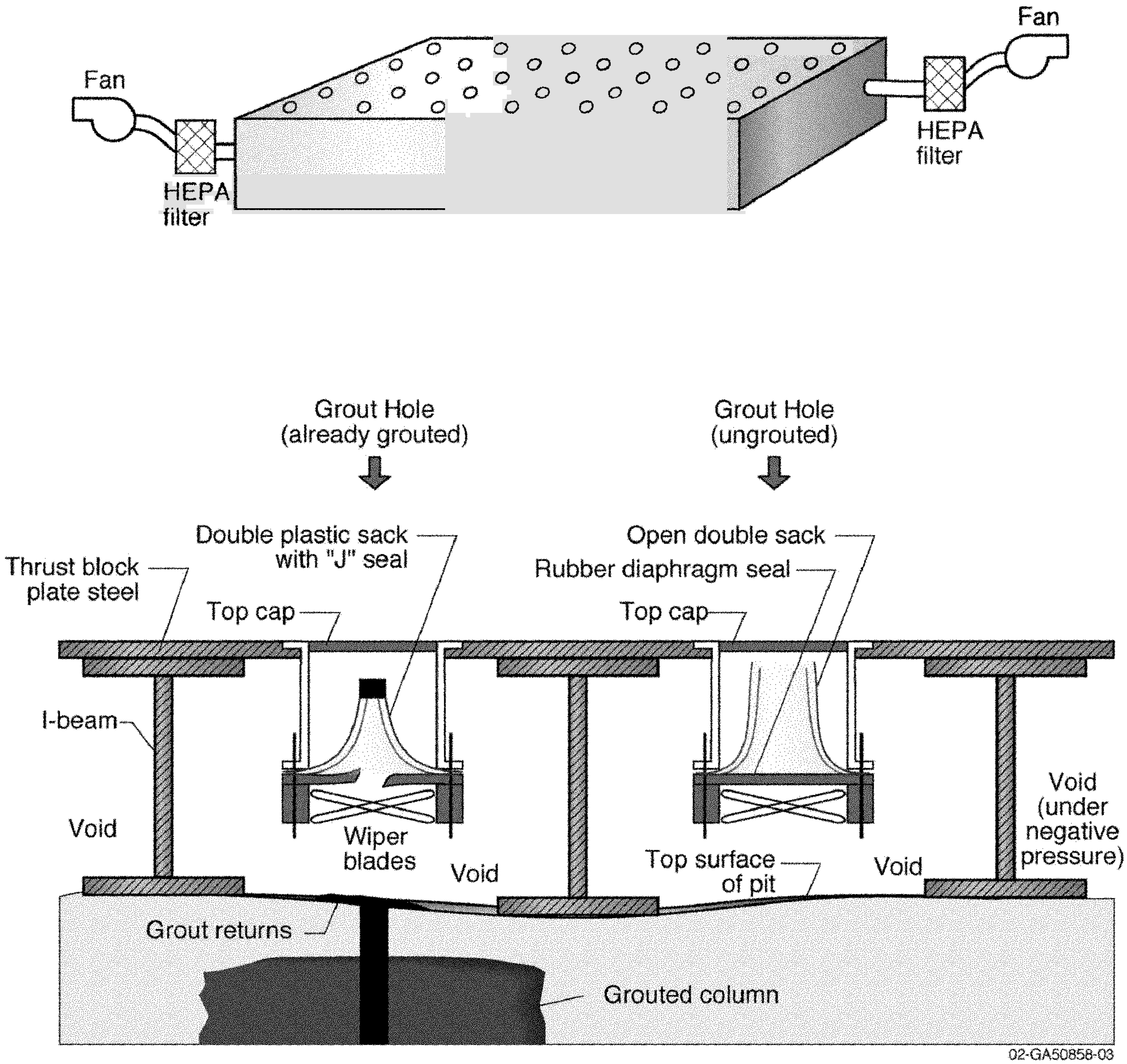

Figure 1. Thrust block design features.

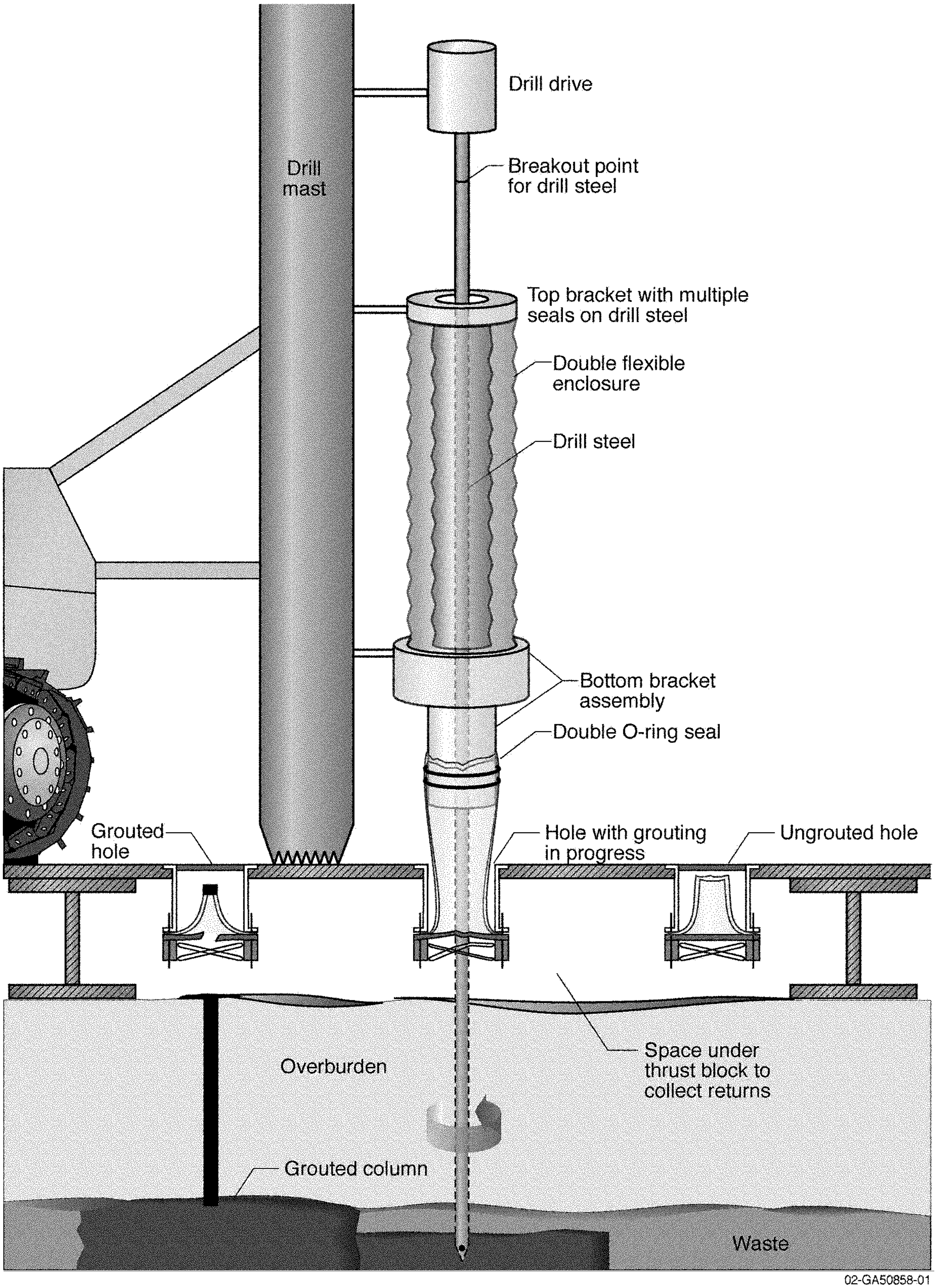

Figure 2. Grouting process with contamination control.

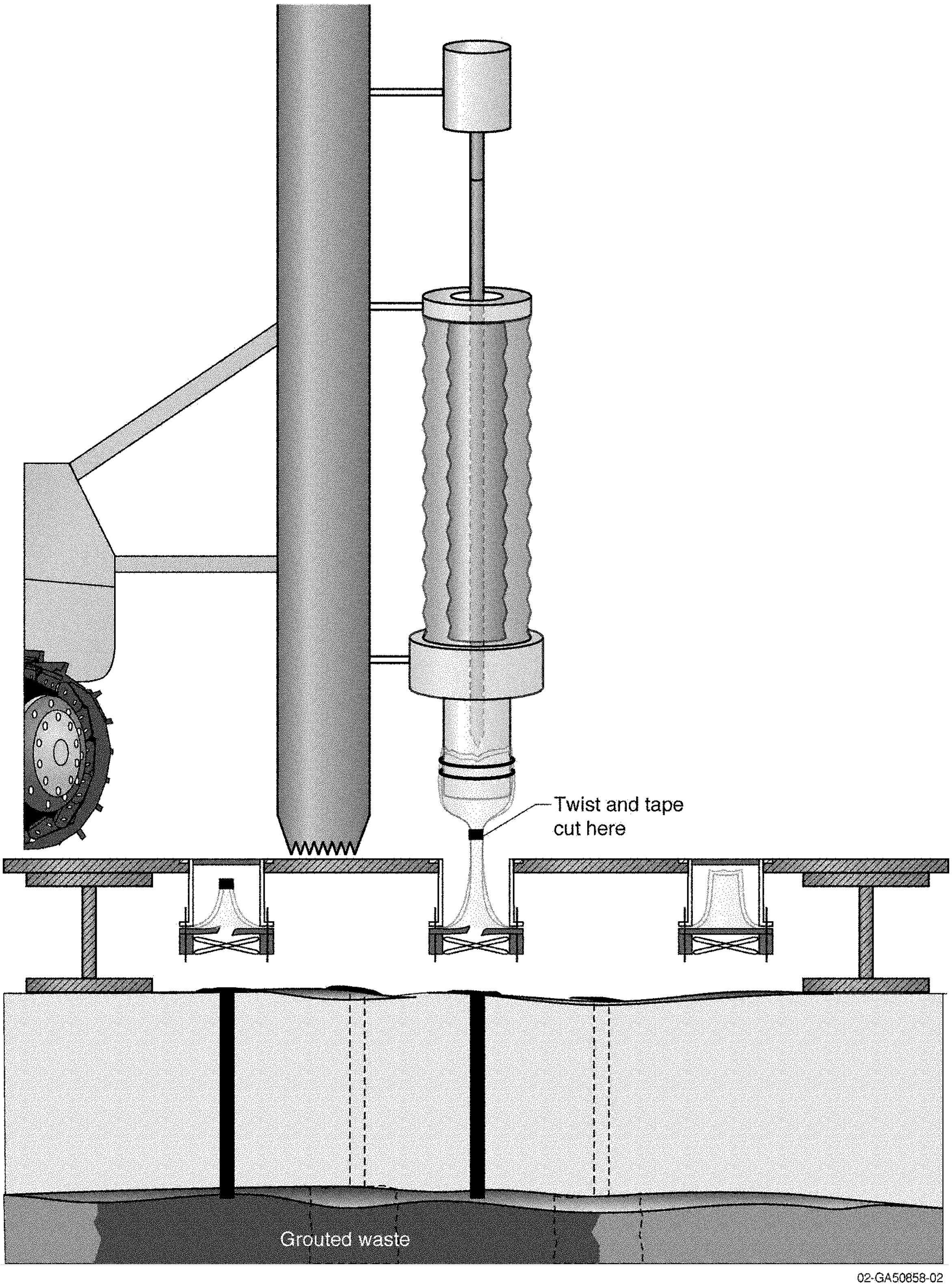

Figure 3. Drill string withdrawn—preparing to move to a new hole.

drill stem into the waste. A typical set of parameters for grouting a variety of single-phase materials includes two revolutions of the drill stem per discrete step (a step is nominally 5 cm), with the step time usually between 2-6 seconds depending on grout returns. It was found that with a balance of these conditions along with specified grout physical characteristics 400 bar pressure created the best commingling of grout, soil, and waste and filling of voids within the waste.

Single-component materials that have been successfully grouted include simple Type-I Portland cement (Loomis and Thompson 1995; Loomis, Thompson, and Heiser 1995; Loomis, Zdinak, and Bishop 1997); Type-H Portland cement (Loomis, Zdinak, and Bishop 1997); TECT, a proprietary iron oxide cementitious grout from Carter Technologies of Houston, Texas (Loomis, Zdinak, and Bishop 1997); and Waxfix, a molten hydrocarbon product also from Carter Technologies (Loomis, Zdinak, and Bishop, 1997). Table 1 shows grout injection data compiled from various INEEL technical reports for these single-phase material studies.

Table 1. Single-component grout injection data.[a]

Grout Type/Pit Type	# Holes	Total Injected Grout (L/gal)	Total Grout Returns (L/gal)	Injected Grout per 30 cm or 1 ft (L/gal)	Reference/Comments
Type-H cement/debris pit	27	11435/3,021	427/113	47/12.5	Loomis 1997—grout mixed 1:1 by volume = 18 sacks/m^3
TECT Carter Technologies/ debris pit	11	4417/1,167	189/50	66/17.6	Loomis 1997
Type-H cement/debris pit	19	5435/1,436	79/21	47/12.5	Loomis 1997—grout mixed 1:1 by mass (= 14 sacks/m^3)
Waxfix Carter Technologies/ debris pit	15	4644/1,227	1483/392	51/13.5	Loomis 1997—molten wax @ 60°C (140°F)
Type-I Portland/debris pit	36	18347/4,847	760/201	51/13.5	Loomis 1994—mixed 1:1 by mass; created a monolith for retrieval studies
Type-I Portland/debris pit	52	18347/4,847	435/115	39/10.3	Loomis 1995—grout mixed 1:1 by mass; created a wall barrier for retrieval studies
TECT HG Carter Technologies/ soil only	52	12472/3,295	2759/729	26/7.0	Loomis 1999—Acid Pit stabilization in soil only

a. Nominal injection pressure 400 bar. See first four references for other injection parameters such as drill rotation speed, withdrawal rate, step size, and time on a step.

In general, for pits containing debris, the average amount of injected grout per 30 cm (1 ft) that supported minimal grout returns while creating a solid overlapped series of columns was 42.4 L (11.2 gal). However, when injecting grout directly into soil, the amount of grout is reduced to nominally 2.2 L/cm (7 gal/ft), primarily due to fewer voids in the soil than in debris to absorb the injected grout. However, all of these waste materials were successfully grouted to form cohesive in situ monoliths.

The molten Waxfix material was easily grouted, although approximately 40% of what was injected came to the surface as grout returns. This mandates a required large plenum volume under the thrust block or some other berming technique to contain the returning material. While the cementitious pits would cure (hydrate) in the 24–36-hour timeframe, the pit injected with Waxfix took up to 1 week to cool to a solidified mass.

Once cured, the monoliths were both cored and destructively examined. In general, through examination of the cores and the excavated monolith, it was observed that the jet-grouting process created a monolith free of voids. It was also found that the cementitious grouts such as Portland cement and TECT could not saturate the tightly bound paper products but filled all interstitial voids in the waste containers, thus completely encapsulating these difficult-to-penetrate materials. The jet-grouting action created mixtures of grout and surrounding soil. These mixtures appear to be neat grout, grout intimately mixed with soil, and small inclusions of ungrouted soil.

For the pit grouted with the hydrocarbon Waxfix, all waste materials showed a complete penetration by the relatively low viscosity molten Waxfix—as if the grout had soaked into the material prior to curing (solidifying). For the Waxfix case study, soil inclusions commonly observed in the mixtures of soil and grout were completely soaked in the molten hydrocarbon-based grout in contrast to the inclusions found in the mixtures of soil and grout from the cementitious pits. In addition, waste material such as paper and wood likewise showed penetration by the Waxfix hydrocarbon. Even metallic objects showed a "coating" of hydrocarbon on outer surfaces. This is attributed to the relatively long time for the molten hydrocarbon pit to transfer heat to the surrounding soils. The permeation of the molten material into the waste material and soil continued long after a cementitious grout would cure.

For the INEEL soil conditions used in these studies, the general soil hydraulic conductivity is relatively low (1e-5 to 1e-6 cm/s); therefore, most of the injected molten hydrocarbon remained in the pit and did not tend to migrate to the surrounding soils. In pits where the surrounding soils are more porous, molten material may tend to disperse to the surrounding soils, thus leaving voids in the soil/waste zone. Observations from the destructive examination of the debris pits filled with cementitious grouts indicated that they tended to be extremely difficult to remove. The best analogy is destroying a concrete building reinforced with rebar. The waste pit injected with molten hydrocarbon is an exception, in that the contents of the pit were removed with simple digging.

2.3 Grouting with Dual-Component Material

Three separate two-component materials were jet grouted in simulated waste pits with varying results (Loomis, Thompson, and Heiser 1995; Loomis, Zdinak, and Bishop 1997). The materials included (a) an acrylic polymer from Minnesota Mining and Manufacturing Company (3M) known as Hard 5750 and Soft 5751, (b) a DOE-developed natural analog grout with a natural analog of hematite, and (c) a Carter Technologies-supplied water-based two-part epoxy. Grouting data are shown in Table 2.

The 3M acrylic polymer was found to be fully field implementable; however, the hematite and epoxy products could not be jet grouted without further development. Grouting parameters for the 3M acrylic polymer are given in Table 2. The hard material (3M-5750) was developed to form a hard durable monolith suitable for in situ disposal. The soft material (3M-5751) was created to allow ease in the retrieval process, with the added benefit that contaminants would be agglomerated to a nonaerosolizable size, which would eliminate contaminant spread. Grouting was performed using the CASA GRANDE system as discussed above. However, a separate positive displacement pump was added for the second component; and the drill stem, nozzle, and swivel (coupling between the delivery hose and rotating drill stem) were modified.

Table 2. Two-component grout injection data.[a]

Total Holes	Total Grout Returns (L/gal)	Total A Part (L/gal)	Total B Part (L/gal)
	Hard Polymer Pit (3M 5750)		
18	476/126	2157/570	2187/578
	Soft Polymer Pit (3M 5751)		
15	113/30	1934/511	1934/511

242L or 64 gal/hole of combined A and B Part each pit

Grouting parameters: 3 cm/step; 3 s/step
2 revolutions/step for both pits (6 ft deep holes)

a. Acrylic polymer from 3M hard (5750) and soft (5751).

The drill stem had a dual concentric annulus arrangement such that the two components were delivered into the waste through a dual concentric nozzle at the bottom of the drill stem.

Mixing of the two components occurred in the waste as the two streams of grout encountered the soil and waste.

The 3M polymers consisted of two co-monomers with select benzoyl peroxide and amine additives to start the polymerization process. When mixed with soil, the polymer formed a high molecular weight waste form that had excellent durability results. Laboratory testing on samples of polymer and soil (33% polymer and 67% soil by mass) included hydraulic conductivity measurements; resistance to immersion in water, trichloroethylene (TCE), and alkali; and resistance to wet-dry cycling. The laboratory hydraulic conductivity of the soil/polymer mixture was 2.8e-12 cm/s. This is several orders of magnitude lower than the hydraulic conductivity of concretes. Ninety-day immersion testing and the wet-dry cycling testing indicated negligible change in compressive strength. Following grouting and curing, the pit was cored and then excavated. Cores showed that the polymer had indeed cured, suggesting that the process sufficiently mixed the two components downhole. The cores also exhibited little void space, indicating good waste penetration.

When the pit was excavated, the resultant monolith was freestanding. In fact, it could be moved as a complete unit (approximately 1.8 × 1.8 × 1.8 m [6 × 6 × 6 ft]). Examination of the debris within the monolith showed similar results to those found in the pit injected with Waxfix in that there was considerable soaking of paper, cloth, etc., with the fluid prior to the polymerization process. One drawback to the process is that polymerization is exothermic. Temperatures approaching 140°C were encountered with visible smoke emanating from the grout holes. In addition, although not hazardous, the acrylic polymers emit an obnoxious odor. Mitigation of both the high exotherm and the obnoxious odor would require reformulation of the 3M product.

Grouting of the INEEL (hematite) and the Carter Technologies epoxy grout as formulated were not field deployable. For the hematite (a two-part mixture of simple slaked lime slurry and an aqueous solution of ferrous sulfate fertilizer), an attempt was made to inject the mixture into a simulated pit. The fact that the INEEL (hematite) material was not field deployable was most unfortunate in that geological media near the INEEL's Radioactive Waste Management Complex, it was noted that iron oxide-rich deposits tended to be stable in nature and not prone to the natural aging process; therefore, by injecting a slurry that cured to a hard form in the interstitial voids within the waste should promote the natural making of hematite out of the soil/waste matrix in geological times. Unfortunately, the slaked lime slurry caused filter caking, which is where particulate in the lime phase tended to separate out in the process of delivery from the high-pressure pump to the drill stem nozzle. This led to system plugging at points where the slurry was at low velocity. Field attempts to alter the viscosity of the lime slurry by adding water failed to eliminate the filter caking, and additional jet grouting using this material was abandoned. The iron sulfate slurry that is the second component of the INEEL (hematite) grout, however, was found to be jet groutable. As a minimum, to make the hematite grout material jet groutable, a new formulation for the lime slurry would be required. Another possible solution is to reformulate the mixture and inject it as a single-phase mixture with a retarded cure.

For the Carter Technologies epoxy, there were two components—an A part and a B part. The B part was simply too viscous to be pumpable, and the entire load was abandoned. It should be noted that in the laboratory this epoxy mixture created excellent monoliths. The lesson learned from this unsuccessful experience is that strict quality control of the various parts of the material must be maintained when converting from laboratory formulations to thousands of liters of material. However, it is possible through more rigorous quality control that the A and B parts could both be jet groutable, since the A part was shown to be pumpable in the CASA GRANDE class system. The epoxy had the desirable property when mixed with soil that there was not an excessive exotherm nor was there an obnoxious odor.

2.4 Grouting as a Pretreatment Prior to Retrieval

Grouting followed by retrieval was performed using three different grouting materials including Type-I Portland cement, acrylic polymer, and the Waxfix product discussed previously.

2.4.1 Retrieval of a Monolith Grouted with Portland Cement

The original jet-grouting operations to form monoliths in simulated buried waste were performed as a pretreatment to the retrieval of buried transuranic waste [Loomis and Thompson, 1995]. It was thought that by grouting the waste, the fine soil particles would be agglomerated and the ultrafine plutonium particulate would be bound in larger pieces of debris and not easily aerosolized during removal operations. If bound sufficiently, it was speculated that retrieval operations could be easily serviced by manned entry into retrieval arenas using bubble suits. Studies involving retrieval with common mining techniques [Thompson et al., 1993] such as misting with water and surfactants on the dig face showed that, at best, during digging and dumping operations contamination control only achieved a 70% reduction in dust spread (this assumes the plutonium and dust move together, which has been suggested [Loomis et al., 1994]).

It was desired to achieve 90% or better reduction in dust spread to allow manned entry during retrieval operations to perform routine maintenance on remote retrieval equipment. The first effort involved creating a monolith in a full-scale 3 × 3 × 3-m (10 × 10 × 10-ft) pit filled with typical 208-L (55-gal) drums and 1.2 × 1.2 × 2.4-m (4 × 4 × 8-ft) boxes containing simulated waste such as cloth, paper, metal, sludge, concrete, and asphalt. In each container was dysprosium oxide tracer as a stand-in for plutonium. The simulated waste was randomly dumped into the pit and backfilled with soil in a manner similar to the actual burial practices in past INEEL disposal operations.

Type-I Portland cement (mixed 1:1 by mass) was injected into the pit on a 0.6 m (2-ft) triangular pitch matrix. Once a hole was grouted, 5-cm (2-in.) diameter thin-walled metal tubes were inserted into each of the just-grouted holes. These tubes were access holes for application of an expandable grout to help break up the monolith and generally facilitate retrieval. Once cured (in approximately 2 weeks), the expandable demolition grout (BRISTAR) was inserted. However, very little demolition of the monolith occurred. It was determined that the BRISTAR material only correctly operates in a fairly narrow temperature band. Due to the heat of hydration of the monolith when curing, temperatures as high as 60°C

(140°F) were measured. In the 2 weeks of curing, the bottom contact temperature of each of the 5-cm (2-in.) tubes in the monolith was measured daily; and after 2 weeks, the temperatures equilibrated at about 21°C (70°F). From these data, it was assumed that the entire monolith was at this temperature. This assumption proved false, which led to an improper application of the expandable grout. When applying the BRISTAR, the bottom contact temperature of the holes was used; and even though the holes showed a relatively even temperature, it was not indicative of the temperature throughout the monolith. To correctly apply the BRISTAR would require waiting until internal temperatures in the monolith equilibrated (perhaps months). Use of a more extensive temperature measuring system would have allowed a correct application of the Bristar and most likely expansion and cracking of the monolith would have occurred.

Approximately 200 g of dysprosium oxide tracer material simulating plutonium was placed in each container. The spread of this tracer material was assessed for the grouting and retrieval phases of the innovative grout/retrieval operation. No tracer spread was measured in high-volume air samplers above background for the entire grouting operation. Once the pit was cured and the attempt was made to apply the BRISTAR, the pit was excavated with a standard backhoe using a thumb-lifting attachment.

Retrieving the monolith was extremely difficult and involved dropping the backhoe bucket onto the monolith. The resulting monolith resembled a reinforced concrete building demolition project. Especially difficult were the regions of the grouted 1.2 × 1.2 × 2.4-m (4 × 4 × 8-ft) boxed waste material. An evaluation of filters in air samplers situated around the dig face showed that during the retrieval process as much as a 90% reduction in dust spread over a base case of simply digging in surrounding soils was achieved as long as the clean overburden was removed first. If the overburden was not removed first, the top relatively dry material sloughed off into the pit and caused aerosolization of the soil, which was picked up on the high-volume samplers. The tracer material (dysprosium oxide powder) was measured on the high-volume air sampler filters at 1.35 times background for the retrieval activity.

2.4.2 Retrieval of a Monolith Grouted with Acrylic Polymer

Grouting of a two-part polymer was previously discussed. Two versions of this acrylic polymer were grouted, including a "soft-retrievable" version and a "hard-durable" version for disposal. The soft version of acrylic polymer was jet grouted into a simulated pit, allowed to cure, and then retrieved while taking air samples. For the pit grouted with the acrylic polymer, the simulated waste material had as a tracer dysprosium oxide powder at 200 g per container to act as a stand-in for plutonium in an actual transuranic pit or trench. The use of lanthanide oxides as valid stand-ins for transuranic materials has been discussed (Loomis et al. 1994).

During retrieval, evaluation of the air samplers showed a 91% reduction in dust spread; however, the tracer measurement on the air filters showed a two-order-of-magnitude increase over background levels. This was attributed to the fact that an ungrouted portion of the pit was inadvertently retrieved along with the grouted region, thus invalidating the data. The grouted portion of the pit was very easy to retrieve, and no voids were present in the monolith. The acrylic polymer permeated items such as cloth, wood, and paper prior to curing, such that it would be difficult for contaminants to become aerosolized during retrieval operations.

2.4.3 Retrieval of a Monolith Grouted with Waxfix

The monolith created by grouting with Waxfix showed very desirable properties for retrieval of buried waste. The molten material greatly penetrated all positions in the waste pit and agglomerated all fines into essentially nonaerosolizable particles. The retrieval was easily performed with a standard backhoe, and no visible dust was observed. No tracer material was used in the simulated waste containers, nor were dust data taken; however, on a qualitative basis, this material has the potential to greatly reduce dust spread—perhaps as much as 98%.

2.5 Stabilization of the Acid Pit Using Jet Grouting

Following development in cold test sites, the technology was applied to a mixed waste contaminated soil site called the Acid Pit located at the RWMC SDA. This pit contained both mercury at a maximum concentration of 5,200 ppm and minor amounts of fission products and pCi/g quantities of transuranics. Grouting this soil pit was extremely difficult to accomplish without excessive grout returns. While the debris pits could accommodate up to 2.2 L/cm (17.6 gal/ft) without excessive returns, the Acid Pit grouting averaged 0.86 L/cm (7 gal/ft). The operation was successfully completed in that the process was accomplished inside a radiation-controlled zone without the spread of either hazardous or radioactive materials (Loomis et al. 1999). It was estimated that the grouting process filled voids with grout equal to about 25% of the volume of the pit, which is consistent with the void volume in the soil. Based on experience during grouting, it was recommended that, when grouting contaminated soil zones, more grout volume per foot be delivered and more grout collection space under the thrust block be allowed.

2.6 Contamination Control During Grouting

For most grouting demonstrations, contamination control was assessed by evaluation of smears and high-volume air sampling for tracer materials. In all cases, tracer materials were placed in each debris container and generally were the "flour" form of a lanthanide oxide (tracers used included oxides of dysprosium, praseodymium, and cerium). Smears were obtained on the top of the thrust block and on the drill stem, and grab samples were collected under the thrust block. For the smears obtained on the drill stem (under the shroud) and for the grab samples, tracer materials were found to be above background values; however, smears on the thrust block showed no spread of tracer. In previous studies (Loomis and Thompson 1995; Loomis, Thompson, and Heiser 1995; Loomis, Zdinak, and Bishop 1997; Loomis et al. 1999) encompassing grouting with and without use of the thrust block, the high-volume air samplers showed no tracer above background. This was attributed to the simple fact that any contaminant brought to the surface was locked up in a slurry of grout and soil or actually in neat grout returns, and this slurry eliminated airborne release of contaminants.

3. BENCH STUDIES

A complex series of laboratory tests were performed on six promising grouts applicable to the in situ grouting technology. The six grouts were chosen based on either actual past performance in jet grouting applications, or similarities to jet groutable materials for application for supporting disposal of buried waste sites. Although the in situ grouting technology was developed for in situ remediation buried transuranic debris such as what is found in the INEEL SDA it has potential application for supporting in situ treatment of low-level buried waste, as well as retrieval of buried transuranic waste (confinement during retrieval). The ultimate goal of the bench studies is to down-select from the six possible grouts to three grouts to carry into the field during "implementability" testing discussed later.

Desirable properties of the grout for application in buried transuranic waste sites include:

- Durability
- Low hydraulic conductivity
- Low temperature of set
- Chemical buffering
- Physical stability to support a cap
- Administrative feasible (grout availability, nonhazardous components)
- Field implementability
- Grout/interference compatibility
- Volatile organic compounds (VOCs) micro and macro encapsulation.

Properties associated with using in situ grouting for supporting retrieval of buried waste relate to dust control, combustibility during handling, and the evaluation of using boron based grout additives to prevent criticality reactions. Desirable properties for the paraffin-based grout include:

- Neutron absorber compatibility
- Low combustion hazard.

3.1 Background

The six grouts chosen for the bench study were selected from the grout types used during previous in situ grouting investigations at the INEEL (Loomis 1996; Loomis 1999). In these past investigations, grouts that exhibited good implementability tended to have relatively low viscosities, and high specific gravity. Grouts that exhibited initial gel times less than 2-hours caused problems in pumping equipment. Other grouts exhibited particulate separation causing "filter caking" on small jet grouting nozzles. Using these lessons learned, there was an initial screening for the six grouts followed by extensive physical and chemical testing on both the neat grouts and grouts mixed with expected interference materials from the buried waste. Grouts were also selected for compatibility with:

- Conventional jet-grouting techniques
- Environment and geotechnical characteristics of the SDA soil

- Buried waste contaminants and chemistry
- Cost of base materials.

Grouts selected for bench-testing are listed below:

3.1.1 TECT HG

TECT HG is a pozzolanic cementitious grout with proprietary additives from Carter Technologies. TECT exhibited good performance in previous INEEL studies and the HG version of TECT was used for the INEEL SDA Acid Pit project (Loomis et al. 1999).

3.1.2 Saltstone

Saltstone was developed at the Savannah River Site to stabilize aqueous nitrate salt waste streams and associated radioactive contaminants. The grout was specifically designed to stabilize technetium and plutonium. Saltstone is composed of blast furnace slag, fly ash and minor amounts of Portland cement. The grout exhibits acid-base properties (pH) of approximately 9 after set and cure and creates a reducing environment in waste site groundwaters.

3.1.3 Tank Closure Grout

Tank Closure Grout (reformulated as GMENT-12 by Technology Visions) was originally developed at the Savannah River site to stabilize waste remnants in storage tanks. Tank Closure Grout was specifically developed to immobilize uranium, plutonium, and other actinides. The formulation of the grout mix with a specific make up of ASTM Type-V Portland cement, blast furnace slag, and silica fume. The grout exhibits a pH of approximately 9 following set and cure and creates a reducing environment in waste site ground waters. Tank Closure Grout was reformulated by the University of Akron to INEEL jet-grouting specifications to allow jet grouting. Subsequent to the extensive reformulation effort, the grout was renamed GMENT-12.

3.1.4 Waxfix

Waxfix is a proprietary paraffin-based grout tested at the INEEL (Loomis et al. 1996). Waxfix from Carter Technologies exhibited excellent field performance. The molten material penetrated even the smallest void volumes in the pit and provided very low hydraulic conductivity.

3.1.5 U.S. Grout (Ultrafine Grout)

U.S. Grout premium grade is a pozzolanic cement from Hess Products of Malad, Idaho, that exhibits physical properties (low viscosity and delayed set parameters) indicating ease of grouting. It is a mixture of Type-H cement and local Idaho pumice.

3.1.6 Enviro-Blend—American Minerals (Phosphate)

This is a phosphate grout under development by American Minerals, Inc. The presence of phosphate in grout has been shown to result in good chemical fixation properties.

3.2 Test Objectives

The 9 CERCLA criteria provided the bases for all test objectives. Objectives for the bench part of the treatability study were given in detail in the test plan (Grant et al. 2000); however, a major programmatic objective was to down-select from the six grouts to three grouts to carry into the implementability testing discussed in the next section. The CERCLA related objectives included examining the grouts for implementability, overall protection of human health and the environment; compliance with applicable or relevant and appropriate requirements; long-term effectiveness; and reduction of toxicity, mobility, and volume.

3.2.1 Bench Testing

The critical objectives for bench testing outlined in the test plan (Grant et al. 2000) associated with the bench testing include (listed with the same numbering system as shown in the test plan):

Test Objective 1-Estimate the Durability of the Grouted Waste Monoliths

$SrCO_3$ and/or KNO_3 were added to the grout material at 0.1 percent by weight prior to mixing. The cured grouts were subjected to American Nuclear Society (ANS) 16.1 leach testing and the leachates where analyzed for either strontium tracer alone or for strontium tracer and nitrate tracer as well as aluminum, calcium, and silicon depending upon the test phase. Performance lifetime for the test grout mixture(s) in the waste site will be calculated from the ANS 16.1 protocol. This information will provide an estimate of the long-term physical and chemical durability of the grout material and an estimate of the rate of diffusion of contaminant materials from the grout matrix. The release rate of calcium, aluminum, and silicon provides a measure of the dissolution rate of the grout matrix. This information may be used to estimate the time the grout will provide physical stability to the waste-site and will affect the chemical behavior of the waste-site ground water. The release rate of the strontium and nitrate tracer materials will provide an estimate of the release rate of contaminant materials. Because it is not feasible to test all contaminants of potential concern, literature values of most contaminants will be used by the ER risk model. The values for strontium and nitrate measured in this study will be compared to the accepted literature values to provide a standard of comparison for the data obtained in the test program. Dissolution rates will be used to predict the long-term chemical durability of the grout monoliths. The durability estimates will establish the ability of the grout monolith to resist chemical degradation, thus maintaining contaminant encapsulation and chemical buffering.

Test Objective 2—Evaluate the Hydraulic Properties of the Grouted Waste Monoliths

Hydraulic conductivity, tensile strength, set temperature and shrinkage tests were performed on grout samples. The hydraulic conductivity measurement (ASTM D 5084-90) was carried out using the flexible wall permeameter which measured water saturated porous material. Tensile strength was measured by ASTM C-496-96 to determine the splitting tensile strength of cylindrical concrete specimens. Set temperature was measured using a simple thermocouple and data logging system. In the case of cementitious grouts, the set temperature is the temperature maximum during the cement hydration (setting) process. Shrinkage measurements (ASTM-C-827-95) determine the change in height of cylindrical test specimens from the time of casting until the time of set. The measurements include shrinkage or expansion due to hydration, settlement, evaporation, and other effects.

Test Objective 3—Identify Grout Material to Support Monolith Application, Safety Related Objective

Several ratios of soil/waste to grout mixtures were used to determine the maximum matrix/interference-loading ratio. The physical and chemical properties and temperature of set was determined for the grout–soil monoliths. The chemical and physical properties data will be used to evaluate the grout formulations, and to select an appropriate mixture for implementability- and field-phase testing. The temperature of set data determines if the grout/interference mixtures set at a temperature greater than or equal to 100°C. A temperature of set in excess of 100°C may represent a safety hazard due to possible steam generation and expulsion of soil, grout, and waste materials (Loomis 1995).

Test Objective 4—Evaluate the Chemical Buffering Properties of the Grouted Waste Form

The solubility of hazardous waste constituents is affected by the chemical environment. For example, the dissolution of metals is influenced by the pH and oxidation-reduction potential (eH) of the surrounding medium. The pH and eH of the grout formulations was measured in the leachate for the ANS 16.1 leaching testing for both neat grouts and grouts with interference materials. pH is measured using a glass electrode (ASTM D 1293-95) and eH is measured using an inert metal electrode (ASTM D 1498-93). The eH and pH is indicative of the buffered chemical environment produced by the grout monolith and solubility of the encapsulated waste constituents. The solubility of each of the contaminants of potential concern will be computed as a function of eH and pH in an aqueous solution similar to the ground water at the SDA, namely saturated with calcite and in equilibrium with CO_2 in the air. The contaminant solubility data will be used by the ER risk model, in conjunction with other data from the in situ grouting treatability study and chemical literature, to estimate the mobility and release of the waste constituents. The data will be used to evaluate the grout formulations, and to select an appropriate mixture for implementability- and field- phase testing.

Test Objective 5—Evaluate the Physical stabilization of the Waste site to Control Subsidence

Samples of neat grout mixed with interference materials are tested for unconfined compressive strength. The bench data will be compared to the interference test data from actual field samples taken from the monolith during the field testing. The monolith must provide a stable foundation for material placed upon it, including impermeable caps and cover material. Undesirable collapse and subsidence of soils into subsurface voids occurs at the SDA during wet conditions. Soil subsidence affects the hydraulic properties of the SDA by causing ponding of surface water and may lead to an increase in the development of permeable pathways to the waste.

Test Objective 6—Evaluate the Effects of Soil, Organic Sludge and Nitrate Salt on Grout Properties

The interference of soil, nitrate salt, and organic sludge on the concentrations may adversely affect grout performance. This assessment was performed on specially prepared grout samples mixed at various interference loading concentrations of the simulated materials. During field-testing, samples will be collected and evaluated for comparison to bench results using specific interference loadings. This comparison will give confidence in using bench-derived data to evaluate future grout types for application of in situ grouting to buried waste. Test results and observations will be used to determine the waste loading tolerance for the grout materials and the waste mix compatibility of the chosen grouts with contaminants expected in the wastes buried at the SDA.

Noncritical objectives listed in the Test Plan include:

Test Objective B—Evaluate Effectiveness of Grout Encapsulation in Retaining VOCs–Micro and Macro Encapsulation Tests

Grouts when mixed with interstitial soils have the potential to encapsulate and reduce the release of VOCs from buried waste. These quantitative micro and macro encapsulation tests will measure the amount of VOCs remaining in the grout-stabilized simulated organic sludge samples, at various stages of the curing process as well as after cure. Both microencapsulation and macroencapsulation tests using an actual combination of VOCs and mixtures of soil and grout will evaluate in a specially prepared chamber the transport of VOCs from the monolith.

3.2.2 Special Testing

Objectives relating to special testing of grouting material appropriate for supporting special problems of using the paraffin based grouts.

The critical objectives for these studies include:

Test Objective 1—Evaluate the Effects and Implementability of the Boron Additive on the Properties of the Paraffin-Based Grout (Waxfix), Safety Related Objective

Bench-testing was performed to determine the type and amount of boron compound that can be mixed with the paraffin-based grout. Addition of paraffin to waste containing fissionable material may increase neutron moderation and the potential for criticality thereby creating a safety hazard. Boron is commonly used at nuclear facilities to prevent criticality due to its capacity to adsorb neutron. A sample of the paraffin-based grout was heated until liquefied followed by addition of a solution of boron/borate and glycerin. The blended solution was then allowed to cool to ambient temperature. The solidified paraffin-boron matrix was then examined to determine the effects of the boron/borate additive on the physical characteristics of the grout, the maximum achievable boron concentration, and the suspension and distribution of the boron within the paraffin matrix. The data will be used to determine if the paraffin grout-boron mix may be safely emplaced during field operations. The data will also be used to determine the implementability of the paraffin-based grout with boron additive. The data will indicate if the distribution of the boron within the paraffin matrix is sufficient to be effective as a neutron absorber. The test results will also be used to determine the maximum concentration of boron that may be successfully added to the paraffin grout. The data will be used to determine if the introduction of boron to the paraffin grout will allow for the safe emplacement of the paraffin grout mix.

Test Objective 3—Evaluate the Combustion Hazard of the Paraffin-Based Grout (Waxfix), Safety Related Objective

The Department of Transportation oxidizer test will be carried out on prepared samples of paraffin and nitrate salt mixtures to determine the combustion hazard of potential waste material mixtures. Samples have nitrate salt loadings of 12, 25, 50, and 75 wt%. Testing will be performed according to 49 CFR 173.127. The data will be used to evaluate the combustion hazard of paraffin-based grout and nitrate mixtures.

Noncritical objectives for confinement during retrieval for bench testing include:

Test Objective A—Evaluation of the British thermal unit (Btu) Content of the Retrieved Grout Waste Form

A paper study evaluating the Btu content is presented. The study will show the Btu content of the waste form due to addition of the paraffin-based grout. The increase in Btu content due to the addition of paraffin-based grout will be used to evaluate potential ex situ waste treatment options.

3.3 Bench Testing Protocol

Testing was performed at the University of Akron under the direction of Dr. Al Sehn and Dr. Chris Miller (Miller). The bench testing followed a complex protocol involving first screening tests on neat grouts and grouts with interferences followed by specific physical and chemical testing on both neat grouts and grouts mixed with interferences. Other testing included micro and macro encapsulation testing to evaluate the transport of VOCs either intimately combined with a mixtures of soil and grout matrix or macroencapsulated by the same matrix. Finally, special testing was performed to examine technical issues with using a wax-based grout to support either the in-situ disposal option or the retrieval option. Tables 3 and 4 give a summary of testing protocols:

Table 3. Summary of testing of cementitious grouts for bench grout studies.

SCREENING-NEAT GROUTS	Viscosity (Marsh funnel API RB13B-1); Initial gelation/Final gelation (Shear Vane 100Pa/1,000Pa respectively); Pressure Filtration (API RP-10B); Maximum set temp (in situ thermocouple); minimum free water (volume measurement).
SCREENING-GROUT/ INTERFERENCE MIXTURE Soil-0,12,25,50,75 wt% Organic-0,3,5,7,9,12,25,50,75 wt% Nitrate-0,12,25,50,75 wt%	Compressive Strength (ASTM-C-3996)-triplicate measurements for all grout/ interferences that remain cohesive; Temperature of set-taken for one interference concentration for each grout-interference combination; Qualitative Observations: Cracking and fracturing, set retardation, incomplete mixing, swelling and disintegration.
PHYSICAL AND CHEMICAL TESTING-NEAT GROUTS[a]	Viscosity (API-RP-13B-1) triplicate; Density (ASTM D 4380-84) triplicate; Time to set (Shear Vane 100Pa/1,000Pa) triplicate; maximum temperature of cure (In situ thermocouple-based on neat grout cured in an insulated bottle. There was an environment matching a reference temperature of curing of a 50 wt% mixture of soil and the grout being tested for all samples used in physical testing) triplicate; tensile strength (ASTM C 496-96) 5 measurements; compressive strength (ASTM C 39-96) 5 measurements; Hydraulic Conductivity (ASTM-5084-90) duplicate; shrinkage (measured settlement) triplicate; Pressure Filtration (API-RP-10B) triplicate; Leach (ANSI/ANS 16.1 for Calcium, Strontium, Aluminum, Silicon, Nitrate) triplicate with eH and pH measured for each leach.
PHYSICAL AND CHEMICAL TESTING-INTERFERENCE/ GROUT MIXTURE[b] Soil-@50 wt% Organic-@9 wt% Nitrates-@12 wt%	Hydraulic conductivity (ASTM-D-5084-90) duplicate; Density (volume and mass) triplicate; Tensile strength (ASTM-C-496-96) triplicate; Compressive strength (ASTM-C-39-96) triplicate; Leach test (ANSI/ANS 16.1 Strontium only) triplicate.
MICRO/MACRO ENCAPSULATION TESTING FOR VOLATILE ORGANICS	Microencapsulation testing for U.S. Grout, GMENT-12, and TECT HG a neat grout mixture and Rocky Flats Plant organic sludge containing 9 wt% Volatile organics are intimately mixed and the samples placed in a specially sealed chamber and the offgas measured at various times over a 90-day period. Macroencapsulation testing for U.S. Grout, GMENT-12, and TECT HG:A special hollow cylinder is created out of a 25 wt% mixture of soil and grout and the hollow portion is filled with the pure Rocky Flats Plant organic sludge and sealed in place. The system is placed in the special sealed chamber and the offgas is measured with time over a 90-day period.

Table 3. (continued).

SPECIAL LITERATURE STUDY (Activated Carbon as a Grout Additive)	Determine the efficacy of using finely divided activated carbon powder as an admixture to the grouts to adsorb and hold volatile organics present in the buried waste.
a. 0.1 wt% strontium carbonate and 0.1 wt% potassium nitrate added to the neat grout as a tracer. b. 0.1 wt% strontium carbonate added to the neat grout as a tracer.	

Table 4. Summary of testing for Waxfix.

PHYSICAL AND CHEMICAL TESTING-NEAT GROUTS[a]	Viscosity (API-RP-13B-1) triplicate; Density (ASTM D 4380-84) triplicate ;Time to set (Shear Vane 100Pa/1,000Pa) triplicate; maximum temperature of cure (In situ thermocouple in an insulated bottle.-cured in an environment matching a reference temperature of curing of a 50 wt% mixture of soil and TECT HG grout triplicate; tensile strength (ASTM C 496-96) 5 measurements; compressive strength (ASTM C 39-96) 5 measurements; Hydraulic Conductivity (ASTM-5084-90) duplicate; shrinkage (ASTM-C 827-97) triplicate; Pressure Filtration (API-RP-10B) triplicate; Leach (ANSI/ANS 16.1 for strontium, Nitrate) triplicate with eH and pH measured for each leach.
PHYSICAL AND CHEMICAL TESTING-INTERFERENCE/ GROUT MIXTURE[b] Soil-@50 wt% Organic-@9 wt% Nitrates-@12 wt%	Hydraulic conductivity (ASTM-D-5084-90) duplicate; Density (displaced volume and mass) triplicate; Tensile strength (ASTM-C-496-96) triplicate; Compressive strength (ASTM-C-39-96) triplicate; Leach test (ANSI/ANS 16.1 Strontium only) triplicate.
SPECIAL TESTING FOR Waxfix[c] (Neutron Absorber Additives)	Six samples of a mixture of Waxfix and a mixture of sodium tetraborate and glycerin that gives 1 g/L of B-10 in the mixture will be made with three samples gradually cooled to room temperature and three gradually cooled to 5F. For each of the six samples, 5 samples at 5 different axial locations will be taken for Inductively Coupled Plasma-Mass Spectroscopy for boron (the presence of B-10 will be inferred from this value); Department of Transportation Oxidizer Test for samples containing 0,12,25,50,and 75 wt% potassium nitrate (following 49 CFR 173.127); literature review for the Btu content of Waxfix will also be performed and reported.
a. 0.1 wt% strontium carbonate and 0.1 wt% potassium nitrate added to neat grout as a tracer. b. 0.1 wt% strontium carbonate added to neat grout. c. Physical testing as well as Department of Transportation oxidizer test and Btu content testing deferred based on negative results of B-10 concentration testing.	

3.4 Screening Test Results

An initial screening of both neat grout samples and neat grout samples with interferences was performed for the cementitious grouts. The Waxfix grout was not part of this screening process. The screening tests were designed to eliminate those grouts not meeting the minimum criteria from the extensive testing protocol. Data gathered during past in situ grouting operations conducted at the INEEL established that small amounts of certain interferences have severe and adverse effects on the physical and containment characteristics of the grout monolith (Loomis et al. 1996, 1998). The presence of interferences such as volatile organic chemicals, nitrate salts, and soils in the waste material may slow or sometimes stop grout setting and curing reactions. In addition, past experience has shown that some grouts, while promising in the laboratory, are not jet-groutable in the field. All these screening tests support critical test objectives 3, 5, and 6.

Samples of neat grout were mixed according to the mix formulas supplied by the vendor. Grout formulations that required modification to meet these stated implementability criteria included the Tank Closure grout (renamed GMENT-12) and the Saltstone grout. It should be recognized that these nonvendor grouts were not developed specifically for jet grouting operations, thus the required modifications. The changes to the Saltstone grout and the Tank Closure grout were changes in the formulation to provide improved jet grouting capability. Such changes resulted in a better score in the evaluation ranking. The changes mainly altered the set time, maximum temperature during curing, Marsh funnel time, filtration performance, and amount of settlement/bleed water. The objective was to alter these characteristics of the grouts while either maintaining or improving the strength, permeability, and leaching characteristics of the grouts.

Once mixed, samples of neat grout were poured into 3-in. diameter by 6-in. high plastic molds and allowed to cure for 14 days in a special curing environment. The neat grout was cured in a temperature controlled water bath. The water bath temperature was controlled by following the curing temperature of a reference mixture of 50 wt% soil and TECT HG grout. The grouts were evaluated for specific gravity, initial and final gel time, pressure filtration, maximum set temperature, and free water/shrinkage. Table 5 summarizes the data for this initial screening for the neat grouts with the minimum required criteria for each parameter.

Table 5. Screening test results and criteria.

	Grout Product					
Grout Property	GMENT 12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout	Screening Criteria
Specific Gravity	1.84	1.78	1.60	2.16	1.65	
Viscosity (Marsh Funnel Time) (sec.)	56	165	110	113	58	< 420
Initial Gelation Time (hours)	4.9	9.4	1.8	6.0	4.7	> 2
Final Gelation Time (hours)	10.7	27.5	8.3	17.9	7.6	> 2
Pressure Filtration Coefficient (min $^{-0.5}$)	0.072	0.077	0.023	0.008	0.033	0.1 to 0.6
Maximum Set Temperature (deg. C)	59	32	28	62	46	< 100
Settlement/Shrinkage (%)	1.82	3.16	0.25	0.44	0.84	minimized

Examination of Table 5 shows that for every screening performance criteria the grouts GMENT-12, Enviro-Blend, TECT HG, and U.S. Grout, passed. The only grout that did not meet the minimum requirements was the Saltstone grout in that the initial gel was below 2 hours. This property eliminates Saltstone from further consideration for the treatability study in that a too early set is incompatible with expensive pumping equipment which could "freeze" with early setting grout. With some further laboratory manipulations, it is thought that Saltstone grout could achieve an initial gel time above 2 hours by applying common set "retarders" such as lignosulfanates. However, as formulated it was removed from further consideration for the present application (it is noted here that certain long term testing was performed on Saltstone and is reported in this document; however, as formulated it cannot be considered for jet grouting applications).

3.5 Screening of Grout/Interference Mixtures

In general, the jet grouting process creates a solid monolith. However due to certain interferences there may be regions in the solid monolith that are pockets of mixed neat grout and loose buried waste material. Examples of loose material include interstitial soil, inorganic sludges (that for all practical purposes look like soil both physically and chemically), organic sludges, and nitrate salts. All of these loose materials or interferences can degrade the structural integrity locally within the monolith. As part of the Bench study then, mixtures of grout and interferences were created to further screen the grouts in that if a grout had virtually no tolerance for maintaining its integrity represented by compressive strength at any loading of interference, that grout could be eliminated from further consideration. What follows are experimental results of the effect on compressive strength for three common interferences. The results are tabularized in Table 6. Appendix B has the detailed data sets for the averages shown in Table 6. The data was taken as a set of five measurements for each interference wt%. Five data points provide a reasonable statistical average for compressive strength.

Table 6. Average compressive strength in psi for the interference tolerance testing specimen groups.

		Grout Product				
Interference Type	Interference Percentage	GMENT 12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
None		7,639	150	1,306	6,320	2,582
INEEL Soil	12	5,884	62	1,259	4,150	3,896
INEEL Soil	25	6,048	26	910	3,654	3,098
INEEL Soil	50	2,529	43	1,318	1,924	1,278
INEEL Soil	75	NA	NA	403	NA	805
Nitrate Salts	12	3,171	39	700	3,239	4,801
Nitrate Salts	25	2,885	4	403	1,193	1,383
Nitrate Salts	50	3	NA	1	NA	1,813
Nitrate Salts	75	104	11	3	NA	869
Organic Sludge	3	7,349	133	1,275	4,296	3,276
Organic Sludge	5	6,100	132	1,075	3,706	2,878
Organic Sludge	7	6,215	102	985	2,820	2,644
Organic Sludge	9	6,083	105	1,021	2,618	3,136
Organic Sludge	12	NA	116	924	2,347	NA
Organic Sludge	25	NA	NA	507	204	NA
Organic Sludge	50	NA	52	NA	7	NA

NA – Generally could not form a "stand-alone" monolith.

3.5.1 Soil as an Interference

Mixtures of neat grout and INEEL soil (sieved to 50 Mesh) were mixed at 12, 25, 50, and 75 wt% soil and allowed to cure in 100% humidity environment. It was thought that in a "free standing" monolith in a field application this range of soil/grout mixtures would cover the expected range in the actual jet grouting of buried waste. Considerable tolerance to soil loading was observed; however, for the Enviro-Blend grout, the values all were below 100 psi. Examining Table 6, shows that the individual triplicate test results for neat grout and soil at 12,25,50 and 75 wt%, the GMENT-12 had the highest neat grout compressive strength values which generally continued when adding interferences. Even with 50 wt% soil loadings, the GMENT-12 had compressive strength for the triplicate measurement higher than 2,500 psi, which was higher than the neat Saltstone grout. There was an interesting aggregate effect for the GMNET-12 grout in that the average compressive strength for 50 wt% is higher than for 25 wt% much like adding aggregate to concrete in the building industry. Enviro-Blend had such low initial neat grout compressive strength that any addition of interferences degraded the grout to a condition of not being able to "stand alone." Since soil is pervasive throughout a waste pit and further that during jet grouting one of the main binders for the monolith will be the resultant mixtures of soil and grout, the Enviro-Blend grout as formulated does not pass the screen for tolerance testing. However, GMENT-12, Saltstone (note: Saltstone was eliminated during the neat grout screening in section 2.3 for short set time, however, considerable simultaneous data was obtained and thus will be reported herein), TECT HG and U.S. Grout all met competency soil requirements for 50 wt% tolerance testing. From these data it was recommended that 50 wt% soil be used during the physical and chemical testing for grouts with interferences described in a following section. In addition, 50 wt% soil represents a typical condition found throughout a monolith created by jet grouting a buried waste site.

3.5.2 Organic Sludge as an Interference

Organic sludge when mixed with neat grout during the jet grouting process has the potential to produce zones of considerably degraded grout (higher hydraulic conductivity, loss of compressive strength). On an average in the INEEL SDA transuranic pits and trenches organic sludge makes up about 5vol% of the waste pit volume; however, zones of almost total organic sludge drums are possible. Past studies (Loomis et. al. 1996) have shown that jet grouting grease-like materials can degrade grout curing and monolith stability; however, with certain grouts, when isolated drums of organic material are jet grouted cohesive monoliths can be formed. Grout was mixed with an organic sludge formulation based on Rocky Flats waste (see Table 7) using trichloroethylene, tetrachloroethylene (PCE), carbon tetrachloride (CCl4), and trichloroethane (TCA) as volatile organics mixed with absorbers and TEXACO REGAL MOTOR OIL. The resultant mixture of volatile organics, oil, and absorbers exhibit a grease-like consistency. Once mixed with neat grout and allowed to cure in a 100% relative humidity curing room, the resultant monolith was tested for compressive strength in triplicate at 0, 3, 5, 7, 9, 12, 25, 50, 75 wt% sludge.

Table.7. Material proportions for the organic sludge interference mixture.

Ingredient	Quantity
Calcium Silicate	4120 grams
Oil Dri	620 grams
Carbon Tetrachloride (CCl_4)	2680 milliliters
Tetrachloroethylene (PCE)	740 milliliters
Trichloroethylene (TCE)	740 milliliters
Trichloroethane (TCA)	1030 milliliters
Texaco Regal Oil, R&O 68	5130 milliliters

For GMENT-12, Saltstone, TECT HG, and U.S. Grout, there was good tolerance to organic interferences for lower wt% of the organic sludge (up to 9-12 wt%) as shown in Table 6. However, for higher than 9-12 wt% organic loading, the resultant monolith exhibited low compressive strength. As with the soil interference, the Enviro-Blend grout showed low tolerance for organic sludge at all sludge loadings. Table 6 summarizes the individual test results showing that GMENT-12 had very little degradation and in fact maintained a relatively high compressive strength (nominally 6,000 psi) for all triplicate samples through 9 wt% organic sludge. The TECT HG grout also had reasonably high compressive strength (3,000-4,000 psi) for up to 12 wt% and even tolerated 25 wt% sludge at an average of 2,347 psi, which is consistent with samples obtained during past in situ grouting experiments (Loomis 1996). Saltstone showed an average compressive strength of over 500 psi at 50 wt% sludge. Based on the results shown in Table 6, it was concluded that physical and chemical testing for grouted organic interferences (discussed in a following section) should be performed at 9 wt%.

3.5.3 Nitrate Salt as an Interference

Neat grouts were mixed with granular nitrate salts (roughly 33% potassium nitrate and 67% sodium nitrate representing Rocky Flats evaporation pond salts found in the transuranic pits and trenches at the INEEL SDA.) at various nitrate loadings (12, 25,50 and 75 wt%). Salts in general have been shown to cause degradation of concretes and knowing the tolerance to these nitrate salts is important for determining localized long term monolith integrity. Within local regions around a nitrate drum in a grouted solid monolith, there may be some local degradation due to the presence of nitrates.

Following curing, the compressive strength was performed on the monoliths in triplicate and the average results are presented in Table 6. U.S. Grout showed the best tolerance to the nitrate salts loadings with compressive strength in excess of 800 psi even at 50 wt% loading. Of the grouts that formed cohesive monoliths, the Saltstone grout showed the poorest tolerance to the nitrate salts with virtually no tolerance after 25 wt% loading. Again, as with the other tolerance testing, the Enviro-Blend grout showed virtually no tolerance to interference loadings. Based on the results shown in Table 6, a nitrate loading of 12 wt% were selected to perform physical and chemical testing on the nitrate interference testing. 12 wt% was chosen because it represents the highest nitrate loading that still has structural integrity such as might be found in a monolith near a grouted drum.

3.6 Testing of Neat Grouts

3.6.1 Physical and Chemical Testing of Neat Grouts

Physical testing performed on cured neat grout samples include determining the grout density, viscosity, splitting tensile strength, compressive strength, and hydraulic conductivity as well as the leaching characteristics in water. Chemical testing includes determining the buffering qualities of the grout by measuring pH and eH of leach waters from leaching procedures. The neat grout samples used for physical and chemical testing were cured in a unique temperature controlled bath of fluid rather than exposing the curing samples to supply constant air temperature. This was done to simulate neat grouts curing in an actual buried waste pit in which much of the pit is a mixture of soil and grout. The bath temperature was controlled by using a feedback system in which heat was added to the bath as the reference mixtures temperature of soil and grout increased during hydration or curing. The reference material in this case was 50 wt% soil and 50 wt% grout which is typical of mixtures of soil and grout. The thermocouple in the reference mixtures of soil and grout showed an increase during curing; however, the bath temperature was kept 1–2°F cooler than the curing mixtures of soil and grout. Within this bath, the various neat grout samples of physical cured chemical testing were allowed to hydrate or cure as their nature allowed. This action prevented unwanted physical cracking due to differential heat stresses during the curing process associated with curing in open air.

Physical Testing of Neat Grouts

Table 8 summarizes neat grout properties including specific gravity, viscosity (as measured in a Marsh Funnel), pressure filtration and hydraulic conductivity. There was a considerable range for specific gravity of the various grouts (range 2.16 for TECT HG and 1.60 for Saltstone). Past grouting studies have indicated a tendency for larger column formations for the denser grouts such as the TECT HG. GMENT-12 at 1.85 specific gravity is an intermediate density grout. The Marsh-Funnel test for viscosity showed an average range of 61s for GMENT-12 to 165s for Enviro-Blend. Basically, all of the grouts tested with low enough viscosity to be considered jet groutable.

In past studies, it was found that grouts with as high as 7 min in the Marsh Funnel test could be jet grouted; therefore, all of the grouts are acceptable on the viscosity test. The pressure filtration test suggest that all of the grouts are to be considered stable for jet grouting applications in that the grout does not exhibit a tendency to lose water under pressure when pressed through a filter material. Basically, this means that pressure filtration numbers above 0.4 min (-1/2) are considered unstable mixtures and numbers in the range of .008 to .08 min (-1/2) (which is the range of those tested in this study) are stable and do not bleed excess water under pressure. The hydraulic conductivity values shown in Table 8 are excellent for all 5 grouts tested. GMENT-12 and TECT HG had hydraulic conductivities on the order of e-9 cm/s, which is nearing measurement limitations for the time allowed to perform these studies.

The porosity of the GMENT-12 cured neat grout is estimated by Dr. Al Sehn of the University of Akron at 25%. The porosity of other grouts considered in this study were not measured, in that the technique involves baking the sample thus, introducing cracks in the system (ASTM C 642-97 was called for in the test plan [Grant et al. 2000]).

Table 8. Specific gravity values, Marsh funnel times, filtration test results, and hydraulic conductivity values for the neat grouts.

	Grout Product				
Test	GMENT-12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
Specific Gravity, Test 1	1.85	1.77	1.60	2.16	1.65
Specific Gravity, Test 2	1.85	1.78	1.60	2.16	1.65
Specific Gravity, Test 3	1.84	1.78	1.60	2.16	1.65
Average Specific Gravity	1.85	1.78	1.60	2.16	1.65
Marsh Funnel, Test 1 (sec)	62	164	87	129	49
Marsh Funnel, Test 2 (sec)	63	165	97	141	50
Marsh Funnel, Test 3 (sec)	57	166	103	148	53
Average Marsh Funnel (sec)	61	165	96	139	51
Filtration Test, Test 1 (min $^{-0.5}$)	0.087	0.084	0.024	0.008	0.026
Filtration Test, Test 2 (min $^{-0.5}$)	0.080	0.082	0.023	0.008	0.026
Filtration Test, Test 3 (min $^{-0.5}$)	0.084	0.082	0.024	0.008	0.024
Average Filtration Test (min $^{-0.5}$)	0.083	0.083	0.024	0.008	0.025
Hydraulic Conductivity, Test 1 (cm/s)	8.5E-09	1.6E-07	1.2E-08	9.8E-09	1.7E-08
Hydraulic Conductivity, Test 2 (cm/s)	6.1E-09	1.3E-07		1.7E-09	1.9E-08
Average Hydraulic Conductivity (cm/s)	7.3E-09	1.5E-07	1.2E-08	5.8E-09	1.8E-08

Table 9 presents the compressive and splitting tensile strength values for the neat grouts. For GMENT-12, TECT HG, and U.S. Grout both compressive and splitting tensile strength were relatively high with a maximum compressive strength for U.S. Grout as high as 9,000 psi and for all grouts the splitting tensile strength was in the range of 500 to 700 psi. In sharp contrast, Enviro-Blend had low compressive strength and splitting tensile strength and Saltstone had relatively low splitting tensile strength.

In summary, from a physical testing standpoint, many of the grouts showed excellent properties for application in buried waste. GMENT-12, TECT HG, and U.S. Grout showed good jet grouting properties while exhibiting excellent strength of grout and low hydraulic conductivities.

Table 9. Compressive strength and splitting tensile strength values for the neat grouts.

	Grout Product				
Test	GMENT-12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
Compressive Strength, Specimen A	3040	103	1407	7443	8230
Compressive Strength, Specimen B	2213	85	1457	6566	8442
Compressive Strength, Specimen C	3154	104	1230	7815	9431
Compressive Strength, Specimen D	6463	100	1421	7947	9432
Compressive Strength, Specimen E	7106	104	1400	6922	8564
Average Compressive Strength (psi)	4395	99	1383	7339	8820
Tensile Strength, Specimen A	668	13	126	757	332
Tensile Strength, Specimen B	836	11	156	758	453
Tensile Strength, Specimen C	781	13	86	780	613
Tensile Strength, Specimen D	643	14	166	692	661
Tensile Strength, Specimen E	605	14	138		481
Average Tensile Strength (psi)	707	13	134	747	508

Leaching Data for Neat Grouts

To determine leaching characteristics, the testing protocol suggested in "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, American National Standard ANSI/ANS-16.1 –1986" was followed. This procedure involves immersing the solid grout samples in a series of baths of demineralized water for various specified times over an interval of 90 days. For each of these baths, the leachate waters were tested for specific leached elements, specifically in this case, aluminum, calcium, silicon, and strontium tracer. If there are materials of interest on the surface, they are theoretically washed off in the early baths such that in an evaluation of later baths for the materials of interest, any that show up in the leachate water are there from deterioration or diffusion within the solid samples. For instance if the Diffusion coefficient changes to higher numbers in the later baths, this is an indication of relatively rapid break-up within the water immersion. If the numbers remain relatively constant or only change slightly, this is suggesting a diffusion controlled release of material and the sample is fairly stable. The volume of leachant employed was 2,200 mL, as specified by the ratio of 10 ± 0.2 of leachant volume to external geometric surface area of the specimen. After rinsing the specimens for an initial period of 30 seconds, the leachant was replenished at specified time intervals: for a total of 10 leachate samples. Aliquots of the leachates were analyzed for Sr, Al, Si, Ca, and $N0_3^{-2}$ using inductively coupled plasma (ICP). Recall that the concept is to measure the dissolution of the building block of the grout (Ca, Si, Al) and mobile contaminants represented by Sr and nitrates. Comparison of the rates of dissolution can be used to support modelings of long term durability of a monolith and the rates of contaminant release. The leaching data are presented in terms of diffusivity coefficient and leachability index. Average leachability indices and diffusivity coefficients were calculated for each of the replicate sets. In rough terms, the negative exponent of the diffusivity coefficient is the same as the leachability index. The detailed data are included in Appendix C.

The results of the leaching test were fitted to a semi-empirical mathematical model based on simple leaching rate mechanisms, which permitted the evaluation of an apparent diffusion coefficient and a leachability index, thus providing a measure of the contaminants' mobility in the solidified waste. In the case of Sr, Al, Ca and Si, the rate of leaching was controlled by an initial wash off, followed by diffusion.

The leach test is a semi-dynamic test; that is, the leachant is sampled and replaced periodically. The test method is applicable to any material that does not degrade, deform, or change its leaching mechanism at the temperatures used in the test. In Appendix C of this report, detailed results of the calculations are presented in several ways. The most basic value determined from a leach test is the incremental fraction leached, from which the cumulative fraction leached is calculated. If less than 20% of a leachable species is leached from a uniform, regularly shaped solid, its leaching behavior (if diffusion controlled) approximates that of a semi-infinite medium. Under these conditions the mass-transport equations permit the calculation of an "effective diffusion coefficient" by the expression:

$$De = \pi \left[\frac{an / A_0}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \tag{1}$$

Where

De = effective diffusivity, cm^2/s,

V = volume of specimen, cm^3,

S = geometric surface area of the specimen as calculated from measured dimensions, cm^2, and

$$T = \left[\frac{1}{2} \left(t_n^{1/2} + t_{n-1}^{1/2} \right) \right]^2 \tag{2}$$

Leaching time represents the "mean time" of the leaching interval.

To measure the base amount of Al, Si, Ca, Sn, and nitrates in the solid grout samples, the following analytical technique was followed:

5 mL (12 M) hydrochloric acid was added to the 1 g solid sample in fluon crucibles and mixed thoroughly. A sequential heating process was then carried out for 2 hours at 150°C. They were removed from the heat, when the solution in the crucible was evaporated. After a cooling period, concentrated nitric acid (2.5 mL) was added and the crucibles were then heated at 150°C for another 3 hours. Once removed from heat, 6-7 mL hydrofluoric acid and 0.25 mL HClO4 were added to each crucible and heated for 5 hours until the solution evaporated to near dryness. 2 mL hydrochloric acid were added to each crucible and then leached for 1 hour. The residues were finally dissolved in 0.2 M HCl. The resultant solutions were subsequently used for analysis by ICP and are represented in Table 10 as mg/g of material for the leachate materials of interest, i.e., calcium, silicon, aluminum, and the tracer material strontium, which was added to a concentration of 0.593 mg/g.

Table 10. Element concentration determination for each grout.

	Element (mg/g)		
Grout	Al	Si	Ca
U.S. Grout	7.79	10.69	37.01
TECT HG	7.28	14.87	107.56
Enviro-Blend	4.88	19.08	4.31
GMENT-12	6.91	8.04	91.64
Saltstone	16.48	5.25	46.48

Note: Spiked with Strontium (Sr = 0.593 mg/g) and nitrate (NO3-2 = 0.614 mg/g).

The individual leaching data for each grout are shown in total in Appendix C and Table 11 summarizes the average leach index for the various grouts (note, the Leach Index is approximately the absolute value of the negative exponent of the diffusivity coefficient, therefore, the higher the leach index, the more resistive a material is to leaching).

Table 11 shows the evaluation of leach index for grout specific elements (aluminum, silica, calcium) as well as for a nonradioactive tracers strontium and nitrate salt placed in the grout as a 0.1 wt% of grout mixture strontium carbonate and sodium nitrate. A higher leach index (or smaller diffusion coefficient, which is basically the negative exponent of the leach index-see the Appendix C for a complete listing of diffusion coefficients as well as other data) is an indicator of durability. As shown in Table 11, all grouts exhibited relatively high leach indexes (10-14.5) for all constituents in the grout (aluminum, strontium, calcium, and silicon) with the phosphate containing American Minerals, Inc.'s Enviro-Blend having the highest leach index.

Table 11. Neat grout average leach index (n = 3) results for Sr, Al, Ca, Si, and NO_3^-.

Grout	Sr	Al	Ca	Si	NO_3^-
U.S. Grout	10.6 ± 0.9	11.1 ± 0.4	9.8 ± 0.9	10.2 ± 0.7	9.2 ± 0.3
TECT HG	10.1 ± 0.3	12.3 ± 0.6	10.1 ± 0.5	11.1 ± 0.5	11.0 ± 0.7
Enviro-Blend	12.8 ± 1.2	14.5 ± 1.6	9.8 ± 0.3	14.2 ± 1.5	8.8 ± 0.2
GMENT-12	10.0 ± 0.5	12.2 ± 0.8	10.5 ± 0.5	10.7 ± 1.1	10.4 ± 0.6
Saltstone	10.2 ± 0.6	12.6 ± 0.9	10.5 ± 1.0	10.2 ± 0.9	10.8 ± 0.8

Results reported ± one standard deviation.

As expected, the nitrate material showed lower leach indexes with a range of 8.8 to 11.0, which are impressive considering the solubility of nitrate materials. The Enviro-Blend grout had higher leach indexes than the other cementitious grouts because of the presence of phosphates that form insoluble compounds with leachable material. As an example of a complete data set (the leaching was performed in triplicate for each grout), Table 12 shows the complete data for the TECT HG grout for one replicate sample for the entire 90-day testing (using diffusion coefficient rather than Leach index). Notice in Table 12 that the diffusion coefficient is relatively stable in that there is not a tendency to decrease with further immersion in the leachate with time for all elements except for the nitrate salt as expected. As a further example, during the time period between 47 days and 90 days (a total of 43 days leaching), there was only .664 mg/L of Sr leached (average .015 mg/L per day) compared to the surface wash-off seen in the first few days which is on the order of 0.2 mg/L leached. This suggests that following the surface wash-off effects, the process of elements entering the leachate water is diffusion controlled.

Table 12. TECT HG grout replicate neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.073	0.028	14.097	0.625	0.019
0.292	0.086	0.051	15.697	0.489	0.019
1.000	0.182	0.174	36.784	1.421	0.028
2.000	0.187	0.220	47.850	1.782	0.038
3.000	0.147	0.186	40.863	1.722	0.038
4.000	0.100	0.184	16.329	1.676	0.029
5.000	0.118	0.209	30.554	1.925	0.019
19.000	0.975	0.611	208.154	3.825	1.010
47.000	0.564	0.639	95.820	4.554	1.010
90.000	0.664	0.757	82.308	4.463	0.820
			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	4.33E-11	4.22E-14	4.89E-11	5.04E-12	2.75E-12
0.292	7.82E-11	1.83E-13	7.93E-11	4.01E-12	3.58E-12
1.000	1.04E-10	6.29E-13	1.30E-10	1.01E-11	2.31E-12
2.000	1.35E-10	1.25E-12	2.69E-10	1.96E-11	5.22E-12
3.000	1.43E-10	1.52E-12	3.35E-10	3.10E-11	8.87E-12
4.000	9.26E-11	2.07E-12	7.51E-11	4.14E-11	7.28E-12
5.000	1.66E-10	3.44E-12	3.39E-10	7.02E-11	4.04E-12
19.000	1.40E-10	3.65E-13	1.94E-10	3.41E-12	1.40E-10
47.000	3.40E-11	2.89E-13	2.98E-11	3.52E-12	1.01E-10
90.000	4.23E-11	3.65E-13	1.98E-11	3.05E-12	6.03E-11

Chemical Testing of the Neat Grouts

The in situ grouting materials performance goals include (a) provide physical stability to the waste site (b) inhibit mobilization of contaminants of potential concern by limiting waste site hydraulic conductivity and (c) provide a constant chemical environment so that the solubility of the contaminants of potential concern can be predicted. The durability estimate is based on the dissolution rate of the chemical elements, which constitute the waste stabilization materials, namely the chemical components aluminum, silicon, and calcium. Such an estimate assumes that factors such as the recrystalization of minerals structures within the grout material are negligible in comparison to the rate of dissolution of the waste form and that the SDA climate remains virtually unchanged.

To determine the buffering capabilities of the grout and to determine the chemical compatibility of the grout with the surrounding soils (whether these soils are INEEL silty clay soils or elsewhere), the pH and eH of the leachate water for each bath of the ANS 16.1 testing described above was analyzed. A detailed discussion of how eH and pH relate to chemical buffering of the waste contaminants and long term durability is included in Appendix E. Table 13 summarizes the neat grout pH and eH data from the ANS 16.1 testing.

The range of pH range was measured at 9.6 to 11.2 and the eH ranged less than 390 mV during the 90-day testing. This pH and eH data can be used by computer models that calculate the long-term response of the grout in a flowing water situation.

The chemical properties of the grout material may effect, and be affected, by the chemical properties of the waste site ground water and waste materials. The pH and eH are two chemical properties, which are particularly important. for estimating the behavior of grout materials in the waste site chemical environment. Changes in pH and/or eH can affect the dissolution/precipitation of mineral material and the dissolution/evolution of gasses and also the adsorption/desorption of aqueous species. The pH can affect the solubility of the grout and waste materials by altering the chemical speciation in aqueous solution. PH is defined as the negative logarithm of the hydrogen ion activity. The eH is the electrical potential for moving electrons between oxidized and reduced species in an aqueous solution and is measured in millivolts. eH is important for estimating the behavior of elements, which can exist in more than one oxidation state, such as technetium, chromium, plutonium, neptunium, and americium. Elements such as technetium and chromium are very insoluble in reducing conditions, but become very soluble in a more oxidized environment. Some elements can exists in as many as four oxidation states. Each oxidation state has a different solubility because the oxidation state (and pH) affects the speciation of the element.

The pH and eH of the leachates were measured during the leach tests described above. All grouts produced alkaline, moderately oxidizing solutions having a pH in the range 10.9 (GMENT-12) to 11.4 (TECT HG) and eH of about 225 mV (Saltstone) to 390 mV (U.S. Grout). For comparison the ground water at the SDA is slightly alkaline, at about 7.16 pH, moderately oxidizing, and is in equilibrium with calcite and variable C02 soil gas concentration (Pace and Hull 2000).

Appendix C gives a complete listing of pH and eH during the ANS 16.1 testing for use in modeling the buffering properties of the grout.

Table 13. Summary of pH and eH measurements of the leachate during ANS 16.1 testing.

Grout Name	Range pH	Range eH mV
U.S. Grout	9.7 to 11.2	Less than 390
TECT HG	9.6-11.4	Less than 384
Enviro-Blend	9.6 to 11.1	Less than 375
GMENT-12	10.6 to 11.2	Less than 313

Durability Estimate Based on Leach/eH-pH Data

The "durability" of a waste stabilization material is defined as the length of time through which it will function as designed. For the Subsurface Disposal Area, these results indicate that the properties of the in situ grouting materials will remain virtually unchanged for many thousands of years.

The application of in situ grouting at the SDA will produce tabular bodies of grouted buried waste material two to three meters thick and several meters in length and breadth (this is caused by the sequence of grouting). The monolith will be resting upon basalt bed rock and will be covered with about 2 m of soil and an engineered cap (Armstrong et al. 2002) and will be below the frost line. Typically, soils at the SDA are virtually water-saturated at the basalt soil interface and contain less pore water near ground surface (J. Weidner, personal observation, 1991) with about 25% average pore filling (estimated by Dr. Al Sehn of the University of Akron). The grout monolith will be subjected to virtually no wet-dry or freeze-thaw cycles. The compressive strength and tensile strength of both pure grout and grout with waste materials indicate that the grout monolith will not be affected by seismic events. The remaining grout degradation mechanism is interaction with SDA ground water.

An estimate of the rate of grout erosion by dissolution is computed from leach rate data measured by the ANS/ANSI 16.1 leach procedure. ANS/ANSI 16.1 is a standard test method designed to determine the release rate of contaminants from porous-media waste forms such as cement-based grout used to stabilize waste materials. The AN/ANSI 16.1 procedure measures the dissolution rate of the elements of interest into a specified amount of demineralized water, i.e., pure water, at STP, over specified periods for a total of 90 days.

Under the above assumptions, the time required for 1% dissolution of the known grout components (aluminum, silicon, and calcium) was estimated. This calculation assumed a 2-m thickness for a pure grout monolith, as it would be applied in the field, and using data from the ANSI 16.1 43 day test interval (presented in this report) and the 8.5 cm/year average water infiltration rate at the SDA. Results of the computations indicate that "tens of thousands of years" will be required for loss of 1% of the chemical constituents composing the waste form materials. For example, GMENT-12 would require 15e4 years for one percent aluminum loss, 16.3e3 for one percent silicon loss, and 39e3 years for one percent calcium loss, and SALT STONE grout data indicated 32e4 years for one percent aluminum loss, 13e3 years for one percent silicon loss, and 15e3 years for one percent calcium loss. All the tested grout materials had comparable material loss rates.

3.6.2 Physical and Chemical Testing of Interference/Grout Mixtures

Both physical and chemical testing protocols were performed on cured grout/interference samples consisting of mixtures of neat grout and determined maximum tolerance conciliations of either soil, organic, sludge, nitrate soil. Physical testing including porosity, leach testing, hydraulic conductivity testing, compressive and spitting tensile strength testing. Chemical testing included ensuring eH and pH of the leachate water during ANSI 6.1 leach testing. All samples for physical and chemical testing for the neat grouts mixed with interferences were cured in a special curing room in which the temperature of the room was kept constant at 73.3°F ± 3°F and 100%, relative humidity. This eliminated unwanted differential temperature at the surface of the samples during curing which could affect the results. In an actual in situ case, there would not be surfaces exposed to surface environmental fluctuations during curing.

Physical Testing Results

Porosity. Measuring the porosity of the neat grout interference mixtures (another physical property) was planned. However, the procedure (ASTM C 642-97) called for baking the cured samples which has historically produced large cracks in the samples. Dr. Al Sehn of the University of Akron estimated the porosity of a cured mixture of 50 wt% soil and grout to be 28% for the GMENT-12.

Leach Testing. Table 14 summarizes leach results for interference samples. These leach indexes were not degraded more than one or two orders of magnitude from those shown for the neat grout in Table 11. Even though there was roughly a two-order-of-magnitude change, leach indices on the order of 10, indicate a very durable material.

Table 14. Leach results for interference samples (Leach Index ANS 16.1).

Grout	9 wt% Organic Sludge	12 wt% Nitrate Salt	50 wt% INEEL Soil
U.S. Grout	10.8 ± 0.7	11.6 ± 0.5	11.4 ± 0.8
TECT HG	10.4 ± 0.6	10.6 ± 0.7	10.5 ± 0.9
Enviro-Blend	12.1 ± 0.7	12.2 ± 0.9	12.6 ± 0.9
GMENT-12	10.3 ± 0.6	10.9 ± 0.6	10.6 ± 0.5
Saltstone	10.4 ± 0.4	10.4 ± 0.4	10.5 ± 0.5

Results reported ± one standard deviation.

Hydraulic Conductivity Testing. Table 15 shows the average hydraulic conductivity as measured in monoliths formed by the neat grouts and neat grout mixed with interferences. The testing protocol followed the essence of ASTM D 5084-90. Although there was a marked degradation for samples containing 12 wt% nitrate salts (as much as a two order degradation), there was little degradation in hydraulic conductivity for up to 9 wt% organic interference and 50 wt% soil. It is noted here that a mixture of grout and soil at 50 wt% soil is similar to what is expected in a jet-grouted monolith for the INEEL transuranic pits and trenches. In all cases shown in Table 15, the hydraulic conductivities are extremely low and definitely show an improvement over the ungrouted pits and trenches of around 10^{-5} cm/s (Loomis 1997).

Compressive and Splitting Tensile Strength Testing. Table 16 provides splitting tensile strength values for mixtures of each grout with the various interferences. Table 17 provides compressive strength for grout with interferences. Using neat grout as a baseline (see Table 9), the grouts showed a marked reduction in physical strength from the introduction of interferences. For instance, the Enviro-Blend grout had a very poor neat grout compressive strength (150 psi) and basically low tolerance to any interferences. On the other extreme, TECT HG and GMENT-12 had an excellent neat grout compressive strength (6,320 and 7,639 psi, respectively) and high tolerance to all three interference types. For instance, both GMENT-12 and TECT HG monoliths had robust compressive strength (greater than 1,500 psi) even with 50 wt% soil and 25 wt% nitrate salts. However, both grouts exhibited less by mass tolerance to the simulated organic sludge material (tolerance for GMENT-12 was 9 wt% organic sludge and for TECT HG 12 wt%). The U.S. Grout across the board showed higher tolerance to the interferences. For instance, U.S. Grout could still produce stand-alone monoliths with 75 wt% soil and 75 wt% nitrate salts (refer each to Table 6 which shows the interference tolerance screening test results). GMENT-12 maintained the highest compressive strength in the presence of organic sludge (at 9 wt% organic sludge the compressive strength remained above 5,000 psi as shown in Table 17).

During ANS 16.1 testing for the neat grout samples with interferences (organic sludge, soil, and nitrate salts) each leachate was tested for pH and eH. The results of measurements on interference-material containing samples are shown in Appendix D. The results indicate that none of the interference materials have a significant affect on the eH and pH values. The pH measurements of leachates from grout with interferences materials versus leachate from grout without interferences materials were virtually identical within experimental error. The eH values of the two groups are nearly identical with the leachate from interference material containing grouts having higher values. For example, U.S. Grout leachate has average eH of 245 mV, whereas the leachate from U.S. Grout containing interference materials has average eH of about 405 mV. Both sets of grout leachates are oxidizing.

Table 15. Hydraulic conductivity values in cm/s for mixtures of each grout with the various interferences (cm/s).

Test Specimen	Interference Amount and Type	Grout Product: GMENT-12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
A	12% Nitrate Salts	5E-07	9E-06	2E-08	6E-09	7E-09
B	12% Nitrate Salts	7E-08	6E-06	2E-08	2E-08	2E-08
A	9% Organic Sludge	2E-09	7E-08	4E-08	5E-09	1E-08
B	9% Organic Sludge	4E-09	5E-08	2E-08	1E-09	2E-08
A	50% INEEL Soil	6E-09	7E-07	8E-08	2E-08	3E-09
B	50% INEEL Soil	1E-08	1E-06	8E-08	8E-09	2E-08

Table 16. Splitting tensile strength values for mixtures of each grout with the various interferences (psi).

Test Specimen	Interference Amount and Type	Grout Product: GMENT-12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
A	12% Nitrate Salts	373	5	84	313	256
B	12% Nitrate Salts	258	5	69	296	254
C	12% Nitrate Salts	246	5	95	176	183
D	12% Nitrate Salts	416	4	104	315	190
C	12% Nitrate Salts	413	4	80	376	262
A	9% Organic Sludge	515	19	97	347	187
B	9% Organic Sludge	488	17	93	330	197
C	9% Organic Sludge	513	18	106	241	173
D	9% Organic Sludge	516	19	100	312	152
C	9% Organic Sludge	476	18	98	320	166
A	50% INEEL Soil	308	4	134	313	231
B	50% INEEL Soil	417	3	92	319	257
C	50% INEEL Soil	352	3	161	283	193
D	50% INEEL Soil	359	2	143	328	225
C	50% INEEL Soil	334	3	135	303	201

Table 17. Compressive strength values for mixtures of each grout with the various interferences (psi).

Test Specimen	Interference Amount and Type	Grout Product: GMENT-12	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
A	12% Nitrate Salts	5057	28	662	3034	4364
B	12% Nitrate Salts	4236	28	621	2256	4378
C	12% Nitrate Salts	4201	25	611	2518	4781
D	12% Nitrate Salts	6273	27	646	1556	3522
C	12% Nitrate Salts	5149	28	653	2553	2914
A	9% Organic Sludge	5502	114	973	1987	3147
B	9% Organic Sludge	5375	114	1014	2030	3388
C	9% Organic Sludge	4958	103	1020	1945	3204
D	9% Organic Sludge	5332	123	1040	1994	2843
C	9% Organic Sludge	5842	128	1041	1952	2539
A	50% INEEL Soil	2348	41	1117	1832	2553
B	50% INEEL Soil	3303	45	1030	1895	2405
C	50% INEEL Soil	2376	34	1092	2107	2397
D	50% INEEL Soil	2440	31	1062	1874	2702
C	50% INEEL Soil	2716	28	1050	2178	2617

3.7 VOC Encapsulation Testing

To study the potential VOC migration retardation in a grouted matrix created by jet grouting a buried waste site, microencapsulation and macroencapsulation tests were performed. The microencapsulation simulates the case in which the neat grout is intimately mixed with the waste matrix during the violent jet grouting operation. In this case, the organic sludge described in Table 7 was mixed with the neat grout and allowed to cure. The macroencapsulation case is where a region of VOCs is completely surrounded by a neat grout layer. For this case, a cylinder of neat grout was used as a "macro" and the pure organic sludge was placed inside the cylinder, the end sealed, and the VOC migration was due to diffusion of the VOCs through the surface area of the matrix.

3.7.1 Microencapsulation Testing

Each sample was prepared at 9 wt% sludge and 91 wt% neat grout with the sludge composition given in section 3.5.2 for each of the grouts. Enough grout-interference mix was prepared to allow for the creation of two samples of each of the three candidate grouts at the maximum identified organic sludge loadings. The organic sludge mixture recipe is the same as given in Table 7. The neat grout and VOC mixture were blended and poured into 7.62 cm diameter by 6.35 cm high cylinder molds.

After the cylindrical monolith cured, the monoliths were placed in a specially prepared airtight 305-mL chamber. Within the chamber, the sample was placed in the middle of moist soil to simulate field conditions inside a monolith. This chamber was of sufficient volume to allow removal of small syringes (nominally 5 cc) of air mixed with volatile organic off-gas without compromising the overall gas volume of the chamber. The testing followed a 90-day testing cycle in which the air sample is withdrawn and tested for the four volatile organics every 10 days using gas chromatography for each of the chambers. In addition, in a separate chamber, pure sludge material control was allowed to off gas and similarly tested for the VOCs.

The results of the microencapsulation testing are shown in Table 18 for the three grouts.

When evaluating the offgas of the pure sludge sample in the chamber, there was an essentially instantaneous release (within minutes) for the all of the volatile organics sludges due primarily to a relatively low vapor pressure. This compares to the extremely low offgas rates observed for all of the grouts shown in Table 18.

Examining the data in Table 18, the release rate of the volatile material is extremely low (with the exception of day 10 results) compared to the release rate of just the organic material which is essentially 100% released in a matter of minutes. Day 10 is considered bad data in the evaluation of the air sample across all the grouts and can be thrown out of the data base. TECT HG and GMENT-12 show very consistent results with U.S. Grout showing a slightly better retardation of VOC offgas. For each 10-day testing interval the amount of material released was between 4e-5 to 6e-4 times the source term. To work with an order of magnitude, the amount released is approximately e-5 to e-6 times the source term per day (meaning "hundreds of thousands of days" for complete release). This means that in rough terms, the complete release of the volatile organics in the intimately mixed organic sludge could be retarded for on the order of thousands of years (1,000 years = 365,000 days), which is within the chemical half-life of these materials in surrounding INEEL soils.

Table 18. Gas phase concentration and mass percentage data for microencapsulation test.
(a) GMENT-12

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
0	9.55	2.97	7.39	0.04	0.021	0.023	0.064	BDL
10	135.97	26.36	49.78	0.68	0.299	0.205	0.431	0.005
20	9.16	5.30	7.15	BDL	0.020	0.041	0.062	BDL
30	11.32	10.86	9.13	BDL	0.025	0.084	0.079	BDL
40	10.37	5.10	7.43	BDL	0.023	0.040	0.064	BDL
50	9.10	7.82	7.94	BDL	0.020	0.061	0.069	BDL
60	7.63	3.95	5.83	BDL	0.017	0.031	0.050	BDL
70	6.34	4.92	6.70	BDL	0.014	0.038	0.058	BDL
80	8.08	5.29	6.44	BDL	0.018	0.041	0.056	BDL
90	7.82	5.30	6.72	BDL	0.017	0.041	0.058	BDL

(b) TECT HG

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
0	6.01	2.01	6.38	0.23	0.012	0.014	0.049	BDL
10	25.01	7.67	22.24	0.30	0.048	0.053	0.170	BDL
20	14.17	6.65	11.97	0.13	0.027	0.046	0.091	0.001
30	10.20	6.21	10.39	BDL	0.020	0.043	0.079	BDL
40	12.95	5.40	10.87	BDL	0.025	0.037	0.083	BDL
50	11.14	7.90	11.36	BDL	0.022	0.054	0.087	BDL
60	9.91	4.55	9.10	BDL	0.019	0.031	0.070	BDL
70	6.72	4.85	9.12	BDL	0.013	0.033	0.070	BDL
80	6.25	4.28	7.56	BDL	0.012	0.029	0.058	BDL
90	6.58	4.57	7.80	BDL	0.013	0.031	0.060	BDL

(c) U.S. Grout

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
0	5.90	6.33	9.59	BDL	0.014	0.054	0.092	BDL
10	9.21	6.07	6.67	0.19	0.022	0.052	0.063	0.001
20	4.68	5.09	4.34	BDL	0.011	0.044	0.041	BDL
30	6.30	13.14	6.37	BDL	0.015	0.113	0.061	BDL
40	1.94	2.28	3.98	BDL	0.005	0.020	0.038	BDL
50	2.24	4.18	2.98	BDL	0.005	0.036	0.028	BDL
60	1.92	2.26	2.05	BDL	0.005	0.019	0.020	BDL
70	1.45	2.55	2.43	BDL	0.004	0.022	0.023	BDL
80	1.66	2.54	2.25	BDL	0.004	0.022	0.021	BDL
90	1.52	2.53	2.27	BDL	0.004	0.022	0.022	BDL

Notes:
All values reported are average of three (3) separate samples/bottles.
BDL = Below Detection Limit.
Sample size of 7.62 cm diameter by 6.35 cm height and air volume of 15.42 mL.

3.7.2 Macroencapsulation Testing

Macroencapsulation testing was performed identically to microencapsulation testing only the sample preparation was completely different. For the three grouts used in implementability testing, triplicate monoliths were prepared. The monoliths were prepared by creating a cylindrical sample of neat grout in 7.62 cm diameter by 6.35 cm high cylinders. Immediately after mixing and pouring the soil/grout mixture into the cylindrical sample holders, a 1-in. outside diameter rod was inserted exactly to within 1 in. of the bottom of the sample holder such to allow the rod to remain vertical during the curing process. The samples were allowed to cure 14 days similar to curing techniques used for physical testing samples (i.e., using moisture controls). Once cured, the monolith was carefully removed from the case and the rod withdrawn and the sample inspected for visible cracking due to withdrawal of the rod. The interior of the cavity was quickly hand filled and tamped to within 1 in. ± 1/8 in. of the top with a measured mass of the organic sludge material. The samples are evaluated for TCE, TCA, PCE, and CCl_4. Once filled with sludge, a prepared mixture of quick setting sealant with a special top made of grout was placed in the top 1 in. of the cavity thus sealing the sludge in place. After the top was cured, the monolith was cleaned with a damp rag and placed in a specially prepared airtight chamber similar to that used in the microencapsulation testing. The same testing protocol of withdrawing small amount of gas from the chamber at regular intervals that was used in the microencapsulation testing was used for the macroencapsulation testing.

Data from the macroencapsulation tests are shown in Table 19 with the unexpected result that there is not lower release of VOCs for the macroencapsulation compared to the microencapsulation results shown in Table 18. This was primarily expected because there was certainly a higher concentration of VOCs near the surface of the monolith for the microencapsulation case compared to the macroencapsulation case. In fact, for the GMENT-12 grout there was a general increase in release. Comparing the data between micro and macro tests show that for all cases the TCE tested with the highest release for both macro and micro testing. For the TECT HG grout the macro %age released results are generally across the spectrum of VOCs lower than the micro as expected (macro is generally lower than 0.05% and the micro is generally lower than 0.1%). For the U.S. Grout, there is less of an effect but generally, the macro is slightly lower than the micro tests (macro generally lower than 0.08% and the micro generally lower than 0.1%. However, for the GMENT-12 there is a larger difference than for the other grouts in that the macro test showed a higher release (macro generally lower than 0.175% and the micro generally lower than 0.1%). This increase was certainly not expected in that it was thought that the macroencapsulation would simulate a pure diffusion of the VOCs through the neat grout matrix and thus show a marked decrease in VOCs showing up in the gas volume of the chamber when compared to the microencapsulation results. The explanation for the higher release of VOCs for the GMENT-12 grout for the macroencapsulation tests compared to the microencapsulation tests is due to an obvious crack in the end plug of the samples for this grout as shown in Figure 4. This crack formation was most likely caused by differential curing between the seal material, the top cap, and the basic cylinder itself. Figures 5–6 show less obvious cracking in the base plugs for the U.S. Grout and TECT HG grout, respectively.

Even with the crack in the base plug of the GMENT-12 grout, the release values generally are below 0.175% per 10-day period which equates to a general release rate of e-4 times the source term per day which is still much lower than the instantaneous release form an ungrouted piece of organic sludge material. At e-4 times the source term released per day would equate to a release of 3% released per year or in general, there would be a retardation of VOC flow on the order of 100 years. Of course, for the TECT HG grout and the U.S. Grout, the expected retardation is less than that discussed for the micro tests (i.e., retardation for the macroencapsulation of these materials would be expected to last for thousands of years).

Table 19. Gas phase concentration and mass percentage data for macroencapsulation test.

(a) GMENT-12

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
10	61.88	13.12	26.95	BDL	0.151	0.111	0.281	BDL
20	53.38	21.42	25.63	0.05	0.130	0.181	0.268	0.001
30	33.08	10.73	16.54	6.45	0.081	0.091	0.173	0.058
40	23.28	13.40	13.52	8.31	0.057	0.113	0.141	0.074
50	14.52	19.33	11.38	8.14	0.035	0.163	0.119	0.073
60	5.76	14.02	7.98	6.80	0.014	0.118	0.083	0.061
70	3.33	9.67	4.64	4.85	0.008	0.082	0.048	0.043
80	2.43	16.74	4.16	5.15	0.006	0.141	0.043	0.046
90	0.83	18.74	3.60	4.45	0.002	0.158	0.038	0.040

(b) TECT HG

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
10	2.06	2.71	22.24	BDL	0.005	0.023	0.232	BDL
20	1.24	0.94	2.17	BDL	0.003	0.008	0.023	BDL
30	7.97	2.69	5.62	1.00	0.019	0.023	0.059	0.009
40	1.19	0.75	1.44	0.33	0.003	0.006	0.015	0.003
50	0.93	0.92	1.38	0.39	0.002	0.008	0.014	0.003
60	0.76	0.62	1.29	0.28	0.002	0.005	0.013	0.002
70	0.19	0.37	1.54	BDL	0.001	0.003	0.016	BDL
80	1.03	0.85	1.65	0.40	0.003	0.007	0.017	0.004
90	0.94	0.91	1.98	0.44	0.002	0.008	0.021	0.004

(c) U.S. Grout

Day	CTET (mg/L)	PCE (mg/L)	TCE (mg/L)	TCA (mg/L)	CTET (%)	PCE (%)	TCE (%)	TCA (%)
10	15.48	4.57	8.62	BDL	0.038	0.039	0.090	BDL
20	11.06	2.31	5.66	0.22	0.027	0.020	0.059	0.002
30	13.14	2.94	6.35	0.11	0.032	0.025	0.066	0.001
40	11.04	2.43	6.01	1.11	0.027	0.021	0.063	0.010
50	13.52	4.45	7.38	1.51	0.033	0.038	0.077	0.014
60	9.37	5.26	7.08	7.32	0.023	0.044	0.074	0.065
70	10.12	2.31	6.29	1.28	0.025	0.020	0.066	0.011
80	20.59	5.99	11.53	2.96	0.050	0.051	0.120	0.027
90	15.67	5.63	11.90	2.56	0.038	0.048	0.124	0.023

Notes:

All values reported are average of three (3) separate samples/bottles.

BDL = Below Detection Limit.

Sample size of 7.62 cm diameter by 6.35 cm height and air volume of 15.42 mL.

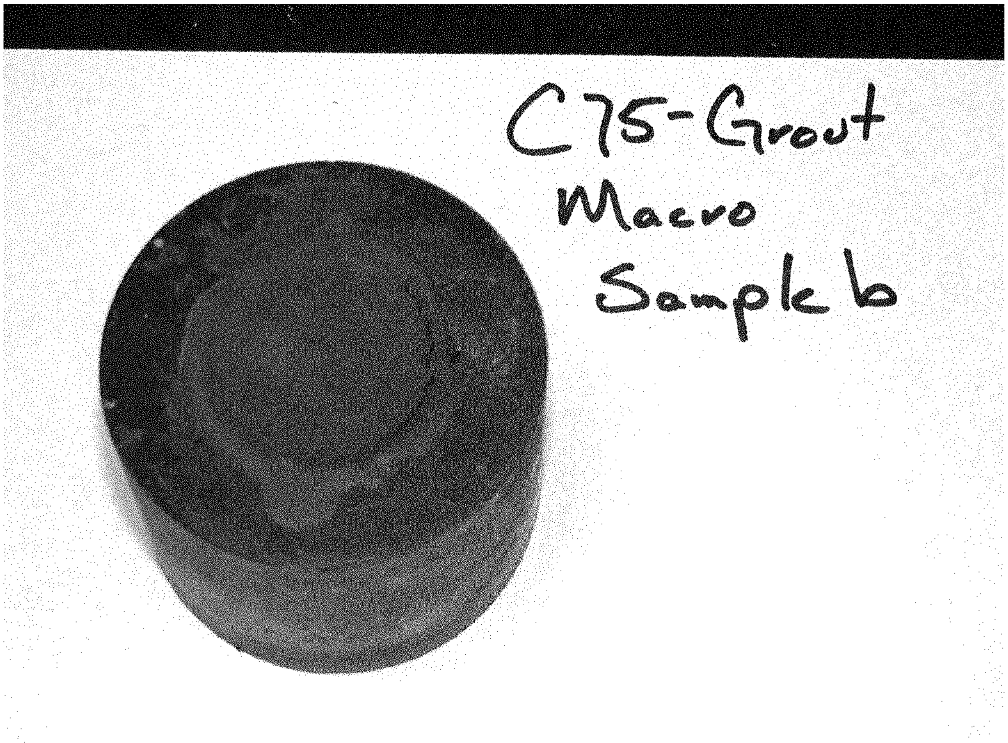

Figure 4. Macroencapsulation cylinder for GMENT-12 (C-75, Tank Closure Grout).

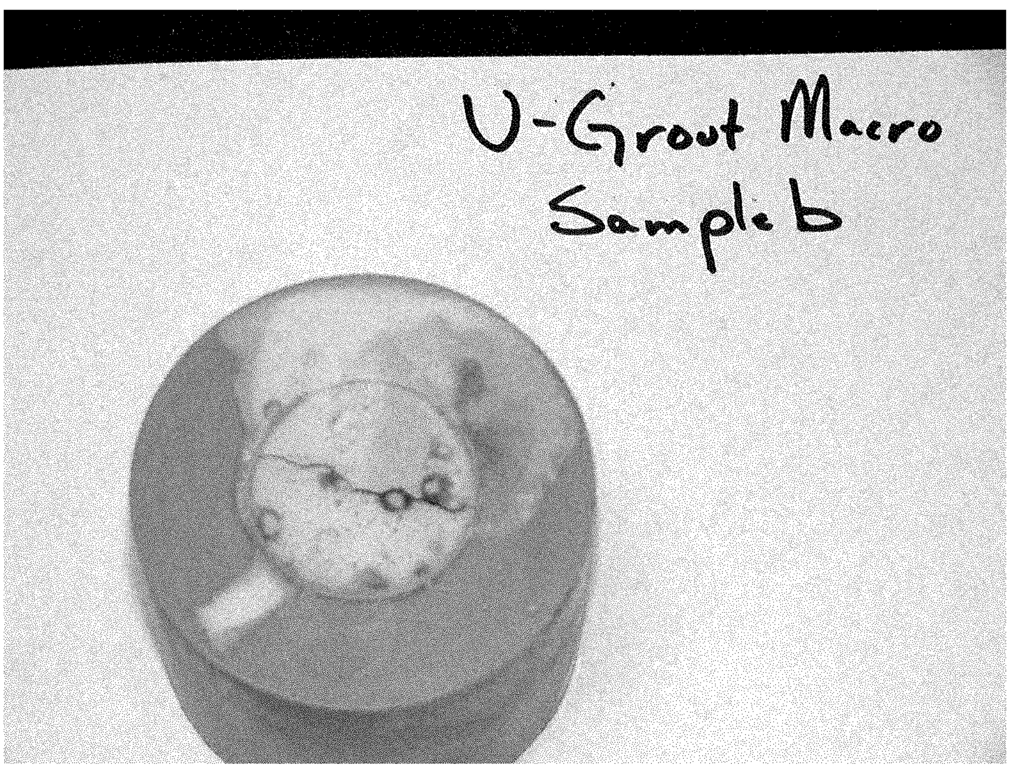

Figure 5. Macroencapsulation cylinder for U.S. Grout.

Figure 6. Macroencapsulation cylinder for TECT HG.

3.8 Special Testing for Wax-Based Grouts

A special testing protocol was performed to examine settling properties of introduced boron compounds in Waxfix. Boron-10 is commonly used in neutron aborber in reactor applications to control reactor criticality. The settling of the boron in the Waxfix is a very undesirable property in that introduction of the Waxfix in a pit containing Pu-239 and U-233 and U-235 raises the possibility of an uncontrolled criticality because of the effective increase in moderation afforded by the hydrocarbon wax increases the potential for a criticality. As an example, the neat Waxfix may fill a box containing a 800g piece of pure plutonium metal and criticality calculations suggest that this is a potential for a criticality. Therefore, the test plan called for a screening test in which a nearly saturated solution of sodium tetraborate in glycerin was mixed with molten Waxfix (140–160°F) such that there was a net 1 g/L of B-10 (the effective boron speciation that has excellent neutron absorption properties). At 1 g/L there was a large safety factor in criticality calculations such that the conservative hypothetical plutonium-239 concentration of particles in a pit would not go critical.

Basically, when correctly mixed and cooled there was a large separation in the boron compounds as shown in Figure 7 during the cooling process. The mixture was allowed to cool down over a multiple day period (5-days), thus simulating the "cooldown" in an injected pit and then examined for settlement by performing ICP-mass spectroscopy (ICP-MS) on samples for boron. Results showed both a strong visual separation of the mixed boron compounds which was in agreement with the ICP-MS results. As an example, the sample was mixed with 56 g of sodium tetraborate per liter of wax and the post cooling

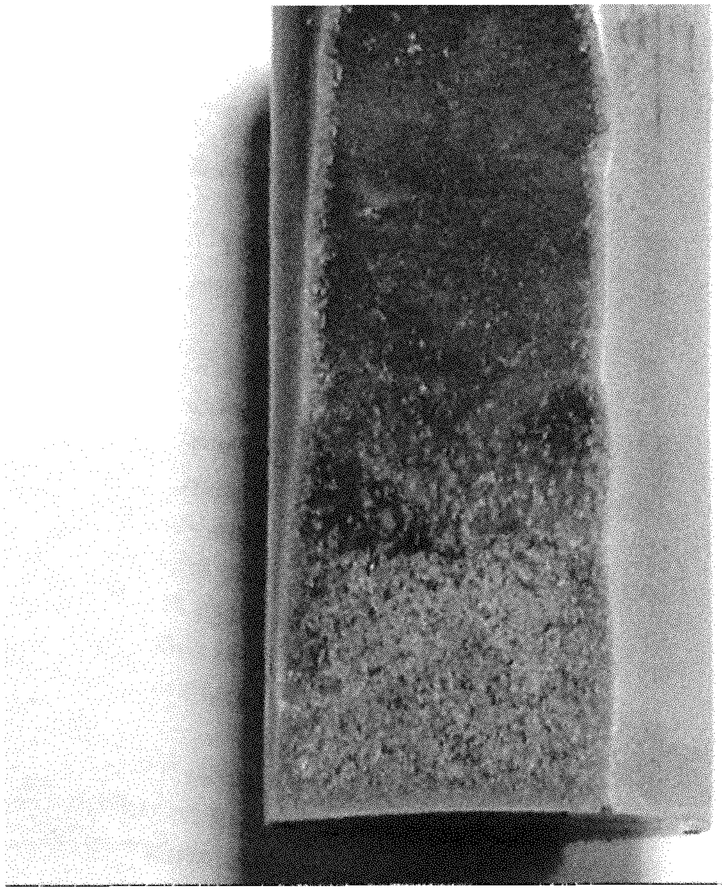

Figure 7. Separation of sodium tetraborate/glycerin during cooling in Waxfix.

separation from samples analyzed with ICP-MS was top of the sample 18mg/L, middle of the sample 43 mg/L and the bottom was 316 mg/L. These results suggest that a completely different introduction scheme be devised to first introduce the boron and then have it stay distributed during cooling.

In summary, it is still possible that the B-10 can be introduced by other means into the cooling Waxfix and still maintain a 1g/L concentration throughout the cooling process. These processes have not been identified in this document; however, are recommended for future work. Because of the negative results for the boron distribution testing, objectives relating to Btu content and combustibility of the Waxfix grout were not performed.

3.9 Use of Powdered Activated Carbon in Grouts

Past studies (Hebatpuria, Vikram et al., "Leaching Behavior of Selected Aromatics in Cement-Based Solidification/Stabilization under Different Leaching Tests," Environmental Engineering Science, Vol. 16, Number 6, 1999) suggested that by adding inexpensive reactivated carbon to cement that there was a significant lowering of the diffusion coefficient for aromatic hydrocarbons under ANS 16.1 leaching protocol. Adding inexpensive reactivated carbon or alternatively activated carbon, to a grout matrix during jet grouting could also increase the leach index and effectively lower the diffusion of volatile organics in the matrix. An analysis of the potential use of powdered activated carbon (PAC) as an absorber for volatile organic hydrocarbons was performed and a complete report on that work is in Appendix B. The basic findings of that work are as follows.

Addition of PAC to the exterior barrier confining the bulk of the waste could reduce the target VOC concentrations at very low concentrations. Using several conservative assumptions, this barrier is expected to be effective for approximately 30 years. After that time, the weakest adsorbed VOC could be displaced by a more strongly adsorbed VOC and the displaced VOC would enter the vapor phase outside the cell. While the 30-year life may not appear good, there are two main reasons to think this may be underestimated by a factor of 10 to 100:

The equilibrium vapor phase concentrations are very high. Including water in the estimates would reduce these values by at least an order of magnitude. Sorption of the VOCs to the solid matrix within the cell could also reduce these concentrations by an order of magnitude. Both these effects would drastically reduce the amount of VOCs being transported to the barrier and the PAC. Vapor phase VOC concentrations need to be determined for the main cell design.

Effective diffusivities of the VOCs in the main cell and within the barrier may greatly reduce the transport of VOCs. The values used were deduced from gas phase values and correspond to transport in soils with 29% porosity. If the main cell and the barrier porosities are smaller and if the materials are retarded in their movement by constant sorption/desorption on the solid matrix, the amount of VOCs transported to the barrier and the PAC would be substantially reduced. Effective VOC diffusivities need to be experimentally determined for the main cell and barrier wall materials.

There is one main reason why the estimate could be optimistic: The matrix surrounding the PAC could block access to the activated carbon microspore surface area and prevent sorption from occurring. This would drastically reduce the sorptive capacity of the PAC and prevent VOC sorption. PAC needs to be imbedded into a barrier matrix and adsorption equilibrium studies determined. In addition, analytical studies should be performed to study using PAC in monolith formation in the waste zone.

3.10 Down-Selection of Grouts for Implementability Testing

The down-selection from five grouts to three for use in the implementability tests involved a unique grading process considering parameters related to the field implementability (jet-groutability), chemical compatibility with the surrounding soils, and durability of the grout once grouted. The list of candidate grouts included Saltstone, Tank Closure Grout, TECT HG, Enviro-Blend, and U.S. Grout. The Waxfix paraffin-based grout and Saltstone were excluded from this selection process during screening testing as described before. The three highest scoring grouts were included in the implementability test program.

Grout Performance Scoring System. The overall performance of an in situ grout material is the sum of the contributions from five performance goals. Because the performance goals do not provide equal contributions to the overall performance of the grout, they are assigned a weighing factor according to their importance. From greatest importance to least importance these include:

- Monolith implementability variables (weighting factor = 5.0)
- Waste site physical stability variables (weighting factor = 4.5)
- Waste site permeability variables (weighting factor = 4.0)
- Grout monolith long-term durability (weighting factor = 4.0)
- Chemical effect of grout material on contaminant mobility (weighting factor = 3.0).

The ranking presented here is based on the assumption that the performance goal is one thousand years and the recognition that these properties are not independent variables.

One or more grout properties affect each performance goal. These include such properties as density, viscosity, cure temperature, hydraulic conductivity, and many others. Each grout property normally has a range of values that may vary from very good to poor. A numerical score is assigned to each acceptable value of each grout property. These are shown in Table 20.

The total score for a candidate grout is obtained by multiplying the performance objective weighting factor times the individual property score, then summing the total number of weighted scores as follows.

$$\text{Total Score for a Grout} = \sum_{I=1}^{n} \text{Property Score (I)} \times \text{Performance Objective Weighting Factor (I)}.$$

The individual property scores assigned to the variables within each performance objective category are based on experience gained from past grouting operations at the INEEL. For example, experience has shown that grout column diameter depends on grout density. In general, higher density grouts produce larger diameter columns of stabilized buried waste. Therefore the denser grout materials are more desirable than less dense grouts and are assigned a higher individual property score. A second example is the set temperature. Low set temperature is more desirable than a higher set temperature because less shrinkage and less cracking are produced and therefore results in lower waste site permeability. In general, an individual property score of 25 was assigned to the least desirable, but acceptable, value of a particular property. An individual property score of 100 was assigned to the best value of a particular property.

3.10.1 Monolith Implementability Variables (Weighting Factor = 5)

Proper monolith development requires high performance from several variables to be successful. Those parameters that affect the implementability of the process include density of the grout, viscosity of the grout, the grout set time and the pressure filtration values. The density of the grout is directly related to column size and thus the ability of the system to overlap columns and produce a continuous monolith without significant untreated zones. Therefore, grout density has relatively high importance. The grout viscosity must be within the appropriate range to be properly injected. If the grout setting time is too fast, or marginally so, the grout could not be injected before set or a coherent monolith could not be produced. Pressure filtration is a measure of the tendency of a particle to stay in suspension and is used to estimate the pumpability of a material. Implementability is the highest priority because it is necessary for the formation of a monolith which stabilizes and encapsulates buried waste in situ.

3.10.2 Physical Stabilization of the Waste Site (Weighting Factor = 4.5)

Physical stabilization is required to prevent waste site subsidence and the resulting ponding and increased infiltration of surface water. Physical stability depends on several variables including low grout viscosity to promote void filling, tolerance of the grout to interference from waste materials and soil, and unsupported compressive strength. The unsupported compressive strength needs to be at least 50 psi or higher (NRC guideline for low-level waste landfills) to support the weight of the over-burden if void filling is not complete. The tolerance of the grout to interference from material such as organic materials, nitrate salts, and soil should be as high as possible to ensure physical stabilization. The viscosity should be as low as possible to promote virtually complete void filling. Note, however, that low grout viscosity

Table 20. Weighting factors and scores.

Performance Objective Grout Property	Weighting Factor	Property Ranges	Property Score
Monolith Implementability Variables	5		
Initial Set Time		2 hr	50
		4 hr	75
		6 hr	100
Density		10 to 13 lb/gal	50
		13 to 15 lb/gal	75
		15 to 20 lb/gal	100
Pressure Filtration		0.5 to 0.6 min	50
		0.3 to 0.5 min	75
		0.1 to 0.3 min	100
Viscosity		7 min	50
		6 min	75
		<5 min	100
Physical Stabilization of the Waste Site	4.5		
Interference Tolerance		Organic at 3%	25
		Organic at 5%	30
		Organic at 7%	40
		Organic at 9%	50
		Organic at 12%	70
		Organic at 25%	80
		Soil at 50%	75
		Soil at 75%	100
		Nitrate at 12%	50
		Nitrate at 25%	75
		Nitrate at 50%	100
Long-term Durability	4		
Accelerated Leach Dissolution		<500 yr	50
		500 to 1,000 yr	75
		>1,000 yr	100
Waste Site Permeability	4		
Hydraulic conductivity		e-6 cm/s	50
		e-7 cm/s	75
		e-8 cm/s	100
Shrinkage		<0.1%	100
		0.1 to 0.5%	50
		0.5 to 1%	25
Porosity		0 to 5%	100
		5 to 25%	75
		25 to 50%	5
Temperature of Set		<100°F	100
		<120°F	75
		<140°F	60
		<150°F	50
		<160°F	40
		<170°F	25
Chemical Stabilization	3		
Chemical properties		pH = 8 to 10; eH < 0 mV	100
		pH = 8 to 10; eH > 0 mV	75
		pH > 10; eH < 0 mV	50
		pH > 10; eH > 0 mV	25

is also an important property in the Monolith Implementability category and is not tabulated in the Physical Stabilization category. Physical Stabilization of the waste site is ranked only slightly lower than Implementability because Implementability is mandatory. Physical stability is ranked as the next most priority performance objective. Long-term Durability and Waste Site Permeability are also very important and are ranked nearly as high as Physical stabilization. Because Physical Stability of the site is required before Waste Site Permeability as a function of time or Long-term Durability can be considered, Physical Stability was assigned a higher value than these two categories.

3.10.3 Long-Term Durability (Weighting Factor = 4)

The long-term durability of the treated waste site is required to be 1,000 years or more. The long-term durability is the length of time that the grout will provide physical stability to the waste site, i.e., prevent subsidence or change of ground surface contour and/or control/buffer the site chemistry. Because the monolith is below the affect of frost, the grout degradation mechanism is dissolution to cause eventual collapse of the monolith. An absolute value for the long-term durability of the grout materials is difficult to determine. For assigning a relative durability value to the different grout compositions, the accelerated leach test will be used. The tests will provide conservative, relative dissolution rates of the grout materials under controlled laboratory conditions. It is understood that these dissolution rates are expected to be higher (much more conservative) than the actual dissolution rate of the grout materials when measured in SDA ground water saturated with calcite and atmospheric CO_2. Long-term durability is given slightly less priority than physical stability. The reason for this is that a lack of physical stability would allow unacceptable system degradation to occur within a few years if the ground surface contour collapsed and allowed ponding and infiltration of surface waters.

3.10.4 Waste Site Permeability (Weighting Factor = 4.0)

Reduction of the permeability of the buried waste site is an important mechanism to reduce the mobility of water borne and soil gas borne contaminants. The grout materials will be ranked according to hydraulic conductivity, the lowest hydraulic conductivity being most desirable. Variables related to waste site permeability are the grout temperature of set and grout isothermal shrinkage. In general, the lowest waste site permeability occurs when the grout material has low set temperature and low isothermal shrinkage, and therefore minimum crack formation. Low permeability grout is judged to have virtually the same priority as long-term durability because the primary goal of long-term durability is to provide long-term physical/chemical stability and thus minimize water infiltration into the waste. Low permeability becomes important when significant water can infiltrate the treated waste.

3.10.5 Chemical Stabilization (weighting factor = 3.0)

The composition of the grout may affect the chemical properties of the ground water and the chemical stabilization of potential contaminants. In general, the most desirable aqueous environment for the stabilization of uranium and other actinide contaminants in SDA ground water is one that has a pH of 8 to 10 and reducing conditions. Least desirable is one that has a pH greater than 10 and oxidizing conditions, equivalent to air. Chemical Stabilization is judged to have lower priority than Waste Site Permeability because the achievement of low permeability restricts contaminant movement to diffusion only and affects both volatile and nonvolatile contaminants.

3.10.6 Numerical Value of the Down-Selection

The down-selection for the cementitious grouts were based on the physical properties of the grout such as compressive strength, hydraulic conductivity, and leach resistance, and jet grouting properties such as set history, temperature of set, viscosity, density and pressure filtration, all applied to a weighting criteria defined in the test plan. Table 21 presents the measured values and raw score for the measured grouts, and Table 22 presents the final score for the cementitious grouts.

Discussion of Scoring for the Various Grouts

Comparison of the four cementitious grouts (see summary Table 23) that passed the initial screening (recall that Saltstone did not meet the minimum screening criteria) show that the relative scoring for U.S. Grout (4150), TECT HG (4184), and GMENT-12 (3862) was relatively close while the Enviro-Blend (3010) was clearly a distant fourth. As expected, Enviro-Blend achieved a better leach index than any of the other grouts because of the presence of phosphate, but the other grouts were high enough in leach index and yet still have all the other desirable properties that the scoring came out higher. In fact, Enviro-Blend had virtually no resistance to interference tolerance and a relatively high shrinkage number such that a zero score was achieved for those parameters. Also, evaluation of the Waxfix paraffin-based grout was halted due to difficulties in achieving a reasonable distribution of the B-10 during a 5-day cooling period and therefore was also dropped. Therefore, using the agreed upon scoring system established in the test plan, three grouts were recommended for testing in the implementability phase including U.S. Grout, TECT HG, and GMENT-12.

Table 21. Measured values and raw score for the cementitious grouts.

Parameter	Test Data/Total Score (0-100)									
	TECT HG		GMENT-12		U.S. Grout		Enviro-Blend		Saltstone	
Initial Set Time (Hours)	6	100	4.95	82	4.7	75	9.4	100	1.8	(Did not meet minimum requirement)
Density (lbm/gal)	18	100	15.4	100	13.7	75	14.8	75	13.3	100
Pressure filtration (min-.5)	.008	100	.07	100	.03	100	.07	100	.023	100
Viscosity (min)	1.8	100	0.93	100	.9	100	2.7	100	1.8	100
Interference										
Tolerance										
Organic	12%	70	9%	50	5%	50	None	0	12%	70
Soil	50%	75	50%	75	75%	100	None	0	50%	75
Nitrate	25%	75	25%	75	75%	100	None	0	12%	50
(Weight %)										
pLeach ANS 16.1(li)	LI = 10.3	80	LI = 10.6	85	LI = 9.9	75	LI = 12.2	90	LI = 10.6	85
Hydraulic Conductivity cm/s	5.8e-9	100	7.3e-9	100	1.9e-8	100	1.5e-7	75	1.2e-8	100
Shrinkage	0.44%	50	1.82%	0	0.84%	25	3.16%	0	0.25%	50
Temperature of Set Degrees F	144	50	138	60	114	100	89.6	100	82F	100
EH/PH Levels	pH = 11.4 eH = 385 mV	25	pH = 10.7 eH = 193 mV	25	pH = 11.1 eH = 388 mV	25	pH = 10.7 eH = 365 mV	25	pH = 9.65 eH = 197 mV	75

Table 22. Final score for the various cementitious grouts.

Grout Property	Weighting Factor	Score TECT HG	Subtotal TECT HG	Score GMEN T12	Subtotal GMENT12	Score U.S. Grout	Subtotal U.S. Grout	Score Enviro-Blend	Subtotal Enviro-Blend	Score Saltstone	Subtotal Saltstone
Initial Set time	5.0	100	500	81.7	408.5	75	375	100	500	0	0
Density	5.0	100	500	100	500	75	375	75	375	50	250
Pressure Filter	5.0	100	500	100	500	100	500	100	500	100	500
Viscosity	5.0	100	500	100	500	100	500	100	500	100	500
Interference	4.5										
Tolerance											
Organic		70	315	50	225	50	225	0	0	70	315
Soil		75	337	75	337	100	450	0	0	75	337
Nitrate		75	337	75	337	100	450	0	0	50	225
Leach	4.0	80	320	85	340	75	300	90	360	85	340
Hydraulic Conductivity	4.0	100	400	100	400	100	400	75	300	100	400
Shrinkage	4.0	50	200	0	0	25	100	0	0	50	200
Temp of Set	4.0	50	200	60	240	100	400	100	400	100	400
eH/Ph	3.0	25	75	25	75	25	75	25	75	75	225
Total Score			4184		3862		4150		3010		3692*

* Did not meet minimum requirement for set time(set time too fast).

Table 23. Relative ranking of cementitious grouts.

Grout	Relative Rank
TECT HG	4184
GMENT-12	3862
U.S. Grout	4150
Enviro-Blend	3010